Studies in Photoelectron Spectroscopy

by

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To my mother

Chymists', pursue your experiments with indefatigable ardour and perseverance. Give us the best possible Bread, Butter and Cheese, Wine, Beer and Cider, Houses, Ships and Steamboats, Gardens, Orchards and Fields, not to mention Clothiers or Cooks. If your investigations lead accidentally to any deep discovery, rejoice and cry 'Eureka!'. But never institute an experiment with a view or a hope of discovering the smallest particles of matter.

– John Adams

I should like to thank my supervisor, Dr. Stephen Cradock for his advice, encouragement and guidance throughout this work, and Professor E. A. V. Ebsworth for his enthusiastic interest.

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Summary

The thesis describes the He I photoelectron, (P.E.), spectra of the silyl and germyl derivatives of the elements of groups V, VI and VII. The bands of the spectra have been assigned in terms of molecular orbital schemes derived by simple molecular orbital theory. The spectra have been compared to those of their methyl analogues, some already published. The ionisation potentials and band contours have been interpreted in terms of π bonding between the donor atom lone-pair electrons and the group IV atom d orbitals, a situation that cannot occur in the carbon analogues where there are no d orbitals in the valence-shell.

The He I and He II P.E. spectra of some simple fluorosilanes and fluoromethanes have been discussed in terms of such π bonding and the perfluoro-effect, (the stabilisation of σ levels on substitution of hydrogen by electronegative fluorine). Less conclusive evidence for π bonding has been found and the perfluoro-effect has been found to be large.

The P.E. spectra of some silyl and germyl substituted π systems have been analysed and discussed in terms of both ($\pi \rightarrow$ d) π bonding and σ / π hyperconjugation, there being evidence for both types of interaction.

The P.E. spectra of two series of iso-electronic derivatives of silane have been analysed and trends in energy levels discussed in terms of symmetry and π bonding. The degree of π bonding has been found to decrease with the donor ability of the substituent atoms.

Appendix I describes the gas-phase electron diffraction structure determination of silacyclopent-3-ene and its 1:1 dichloro-derivative. The almost regular structure of the ring has been taken as evidence that

trans-annular interactions do not occur although the P.E. spectrum does not agree with this.

Appendix II describes the ^{1}H N.M.R. spectra of the vinyl and allyl derivatives of silane and germane. The second order vinyl region of vinylgermane has been analysed with a computer simulation programme.

Appendix III describes some reactions of trifluorosilylchloride and bromide both of which have been found to be virtually unreactive with Lewis acids, elements and weak bases, but to react strongly with strong bases e.g. ammonia.

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INTRODUCTION

This work involves a study by Photo-electron Spectroscopy of main Group Compounds and organic system derivatives of the Group IV elements, Si and Ge with emphasis on the possibility of (p → d) π back-bonding to Si 3d and Ge 4d orbitals, a subject of considerable interest which has been much reviewed (e.g. 6). As an appendix certain electron diffraction structure determinations, N.M.R. Spectra and reactions of various compounds studied will be given.

Photo-electron Spectroscopy (P.E.S.) is a relatively new method of determining the energy levels of ions, both simple and complex. The method of ultraviolet P.E.S. was developed by Dr. D. W. Turner, the first results being published in 1962[1]. Since then an extensive literature has built up with many review articles[2, 3] and a few books[4,5], notably after the availability of a production photo-electron spectrometer from Perkin-Elmer Ltd. Beaconsfield in 1969 based on Turner's original design.

A description of the photoionization process will be given followed by a brief literature survey indicating some of the applications of photo-electron spectroscopy, a description of the spectrometer being given in the experimental section.

The basic photo-electron emission process involves the interaction of a photon with a molecule with the resultant ejection of an electron. The energy of the incident photons govern the nature of the ejected electron; high energy incident radiation (X rays $\sim$1000 eV) ejecting core (1s) and valence electrons and low energy radiation (U.V$\sim$20 eV) ejecting valence bonding and non-bond electrons. The former is known as Electron Spectroscopy for Chemical Analysis (E.S.C.A.) and the latter as simply ultraviolet Photo-electron Spectroscopy.

Measurement of the kinetic energy of the ejected electrons allows, by difference, the various binding energies in the molecule to be determined, viz.

$$E = h\nu - I \qquad A$$

where E is the kinetic energy of the ejected electron, $h\nu$, the energy of the incident radiation and I the binding energy of the ejected electron in the molecular ion produced by the interaction

$$M + h\nu \rightarrow M^{+} + e^{-}.$$

For A to hold, Koopmans' theorem must be assumed to be valid, that is that during the ionisation process, no electronic rearrangement is assumed to occur in the excited state before the ionisation is complete. That is to say that no account is taken of the contribution to the ionisation energy of the energy of rearrangement of the remaining electrons in the molecular ion produced[7]. Thus by measuring the spectrum of ejected electrons, a molecular energy level diagram for the molecule may be drawn up.

Also describing the nature of the ionisation process is the Franck-Condon principle stating that electronic transitions occur in a short time compared to that for vibrational or rotational transitions. Thus the ionisation process can occur from various defined ground states, (vibrational and electronic), to various defined excited states and as such, relation A should be strictly written as;

$$E = h\nu - I - \Delta E_{vib} - \Delta E_{rot} \qquad B$$

where ΔE_{vib} and ΔE_{rot} are due to changes in vibrational and rotational energy levels. Thus Photo-ionisation can lead to a progression of peaks due to the various changes in vibrational quanta on excitation. The probability of transition between two vibrational levels of a ground state and excited state is defined by its Franck-Condon factor and the

intensity of P.E. bands are governed by the square of this factor[4].

This leads to the two definitions of Ionisation Potential involved in photo-ionisation. The adiabatic ionisation potential corresponds to the difference in energy between the vibrational ground states of the potential energy curves of the excited and ground state species. Thus if there is little change in equilibrium internuclear distance, then the maximum probability of excitation is from the ground state lowest vibrational level to that of the excited state and the energy absorbed will correspond to the adiabatic I.P. The vertical ionisation potential follows from the Franck-Condon principle and takes into account any change in equilibrium internuclear distance on excitation due to removal of an electron. Thus the most probable transition from the lowest ground state vibrational level to a vibrationally excited ionic state gives the vertical I.P. Thus transitions can occur to excited states with similar, larger or smaller internuclear distances. A change in the internuclear distance will lead to a corresponding change in the vibrational frequency of that bond. Removal of a non-bonding electron will have little effect on the internuclear distance and hence on the vibrational frequency. However, removal of a bonding electron will lead to an increase in internuclear distance and decrease in vibrational frequency, while removal of an anti-bonding electron will decrease inter-nuclear distance and increase the vibrational frequency. Thus, depending on the vibrational structure observed in a particular band, so an assignment to ejection of electrons from a specific orbital and the formation of a specific ionic state can be made.

Since literature on P.E.S. first appeared there have been a number of reviews, a recent good one by S. D. Worley[3]. A very brief review

showing some of the applications to chemical problems and theory from 1970 onwards will be given.

Problems involving conjugation in bonding have been common in P.E.S. Whether or not Silicon 3d orbitals are a stabilising influence in the bonding of Silicon compounds has been well studies and reviewed[6] but results from P.E.S. have been conflicting. Interpretations of the spectra of the tetramethyl compounds of Group IV elements have been made by comparison with I.P.s obtained from computed molecular orbitals with Si 3d contribution[8], whereas interpretation on the basis of linear energy trends and the effect of high symmetry exclude them[9]. Energy trend considerations also lead to an exclusion of Silicon 3d orbitals in the bonding of the series $Me_n SiCl_{(4-n)}$, $(Me_2N)_n Si Cl_{(4-n)}$ and $(EtO)_n Si Cl_{(4-n)}$[10], and in the polysilanes; $Si_n Me_{(2n+2)}$[11]. Studies of the silyl halides[12], and pseudohalies[13] using symmetry arguments have lead to concurrent results involving d orbitals. In organo-silicon systems, the study of trimethyl silyl allyl[14] and vinyl[15] systems have shown the occurrence of $(p \longrightarrow d)\pi$ conjugation and of $\sigma - \pi$ hyperconjugation between σ Si - C and π bonds. A study of trimethysilyl haloacetylenes has afforded no evidence for conjugation[16], and similarly studies of vinyl boron compounds have shown only limited conjugation to empty Bp_π orbitals[17]. In dimethyldivinylsilane a splitting of the levels is thought to be due to conjugations of the two π clouds through the Si atom [18], and similarly interactions in tetra vinyl silane[19], and bis (biphenyl) silane[20] have been interpreted in terms of spiro-conjuagtion - the interaction of two mutually orthogonal π systems separated by a tetrahedral atom. Spectra of Group IV hydride transition metal carbonyls[21] reveal no evidence for $(d \longrightarrow d)\pi$ interactions from the transition metal d orbitals and similarly

interpretation of the P.E.S. of methyl manganese carbonyl[22] based on calculations indicates no back-bonding to the methyl group. A study of dihaloethylenes and allyl halides [23,24] has given quantitative estimates of inductive and conjugative effects of the substituents. Trends in Ionisation potentials with changing inductive and conjugative effects of substituents in sulphuryl and thionyl compounds have been interpreted in terms of S 3d orbital involvement[25] this also being involved in the bonding of SO_3[26]. Lone-pair conjugation of nitrogen with the degenerate benzene π system in dimethyl aniline is favourable whereas in the corresponding phosphine it is not[27]. Through space lone-pair interactions have been studied in 1, 4 diazabicyclo - (2.2.2) - octane by analysis of vibrational structure on the lone-pair bands [28] and the spectra of 1 sila and 1 germacyclopent-3-ene afford no evidence for d/π transannular interactions[29].

The best oriterion for the assignment of bands is by fine structure analysis, those of X_2CO (X = F, Cl Br)[30], H_2Y(Y = O,S,Se,Te)[31] and H_3Z(Z = N, P, As, Sb)[32] have been thus assigned, analysis of the vibrational structure of the hydrides being used to find changes in molecular geometry in the excited states. Complex vibrational patterns in NSF[33,34] show its electronic structure to be similar to SO_2 despite the different bond orders. An aid to assignment in compounds containing hydrogen is the Perfluoro effect i.e. on substituting Fluorine for hydrogen in a planar molecule, simple or complex, the σ energy levels are stabilised by 2 - 3eV over the π levels[35,36] due to the high electronegativity of Fluorine. Pauling Electronegativity values have been correlated with σ and π levels of simple halogen acids giving a straight line plot[37]. Orbital correlation diagrams have been used in the assignment of Phosgene

and thio-phosgene[38] and the carbonyl halides[39]. Band Intensities have been of considerable interest and theories of intensity have been developed; high ionisation cross-sections for p electrons being due to favourable interaction with large wave length radiation, while low cross-sections from s electrons are due to less favourable interaction[40]. The 'band-intensity-proportional-to-degeneracy-of-orbital' method of assignment has been used to confirm the cyclo-octagonal structure of Sulphur vapour[42], and also interpret the spectrum of P_4[41].

P.E.S. has recently been used as a method of studying species such as CS[43] and free radicals NF_2, ClO_2, SO_3F and $(CF_3)_2NO$[44], vibrational analysis allowing molecular parameters to be found.

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CHAPTER ONE

The Photo-electron Spectra of some mono and dihalo Silanes and Germanes

Introduction

The halides of silicon and germanium are analagous to those of carbon in terms of molecular structure. The difference in electronic structure is that silicon and germanium have empty d orbitals which are available for π bonding by accepting electrons from donor atoms e.g. the lone-pair electrons on halogens, provided they are of the correct symmetry, as in figure 1. This has the effect of shortening bond lengths to silicon and germanium[1] and increasing the ionisation potential of the lone-pair electrons, by delocalisation, as reflected in the n - π^* transitions in the U.V. spectra of mono and dihalo-silanes[1,2] which are greater than those for the analagous carbon compounds. Recently low diple moments for the silyl halides have been interpreted in terms of (p → d) π bonding[16].

The usual method of describing the bonding in these compounds is by hybrid orbitals, on the central atom, of s and p character being σ bonded by overlap with the halogen p orbitals and the hydrogen 1s orbitals. In order to derive an orbital scheme describing this, the constituent valence-shell atomic orbitals are added together, according to simple molecular orbital theory, to give the molecular orbitals, as in Tables I and II. The monohalides are assumed to have C_{3v} symmetry, the M - X bond lying along the z axis and the dihalides assumed to have C_{2v} symmetry with the C_2 axis along the x axis. The P.E. Spectra of methane and silane[3,4] show two bands, one assigned to the M - H bonding levels and a second at higher energy to the C 2s and Si 3s levels. Thus it would appear that in a formally sp^3 hybridised scheme of bonding, not all individual atomic orbital character is lost, the molecular orbitals only being described as partial mixtures of bonding character, this being

TABLE I

(a) Atomic Orbitals and (b) Molecular Orbitals for MH_3X (M = C, Si, Ge, X = F, Cl, Br, I)

(a)

Atomic Orbital	a_1	e
Mns	/	
Mnp	/	
$Mnp_{x/y}$		/
H1s	/	/
Xn's	/	
Xn'p_z	/	
Xn'$p_{x/y}$	/	/
Mnd	/	//

(b)

M – H anti-bonding	$5a_1$	M – H anti-bonding	3e
M – X anti-bonding	$4a_1$	$Xnp_{x/y}$ lone-pair	2e
M – X bonding	$3a_1$	M – H bonding	1e
M – H bonding	$2a_1$		
Xn's lone-pair	$1a_1$		

TABLE II

(a) Atomic Orbitals and (b) Molecular Orbitals for MH_2X_2, (M = C, Si, Ge, X = F, Cl, Br, I)

(a)

	a_1	a_2	b_1	b_2
Mns	/			
Mnp	p_z		p_x	p_y
H1s	/		/	
Xn's	/			/
Xn'p	/			/
Xn'p	/	/	/	/
Mnd	//	/	/	/

(b)

	a_1	a_2	b_1	b_2
Xnp π lone-pairs	$4a_1$	$1a_2$	$2b_1$	$3b_2$
M - X bonding	$3a_1$			$2b_2$
M - H bonding			$1b_1$	
Mns	$2a_1$			
Xn's	$1a_1$			$1b_2$

described in molecular orbital theory by overlap integrals. Thus the silicon 3s and germanium 4s orbitals have been considered as separate although they will be involved in the general bonding scheme, the t_2 M – H bonding orbital of MH_4 splitting to a_1 and e levels in MH_3X.

In the monohalides, the atomic orbitals combine to give 3 x a_1 and 2 x e molecular orbitals of which the $2a_1$ is considered to be mainly Mns in character. Of the atomic orbitals on X, the p_z can easily combine with the Mnp_z orbital, also of a_1 symmetry, to give the $3a_1$ M – X σ bonding orbital, while the p_x and p_y orbitals on X form the degenerate 2e lone-pair orbital. The p_x and p_y orbitals on M combine with the hydrogen 1s to form the degenerate 1e M – H bonding level. For the chlorides, the $1a_1$ Cl 3s lone-pair occurs at high I.P. and will not be detected.

The dihalides require a more complex analysis and belong to the point group C_{2v}. Here the p atomic orbitals of the halogens have been divided into two sets, p_π and p_σ for ease of description. The p_σ orbitals are considered as forming the σ bonds to M, lying along the M – X bond, and the p_π to be formally lone-pairs on the halogen atoms. The p_σ orbitals combine with the p orbitals on M to form bonding molecular orbitals. Bonding to hydrogen is through the directional Mp_x orbitals and to the halogens through the Mp_y orbitals, while the Mp_z and Mns orbitals are involved in both sets. Thus there should be four lone-pair bands, one of each symmetry class, and four σ bonding levels, one with appreciable Mns character. The fourteen electrons for the 3 x a_1 and 2 x e levels of MH_3X are supplied as four from the M, three from hydrogen and seven from the halogen. Similarly the twenty electrons for MH_2X_2 are supplied as two from hydrogen, fourteen from the halogens and four from the M.

Spectra and Assignments

The spectra are shown in Figures (III to X) and the vertical ionisation potentials in Tables (III) and (IV), together with the values for the carbon compounds[6]. Consider first the mono-halides. The spectra of the silicon and germanium compounds are very similar, but the fluorides differ greatly from the other halogens and are considered separately, this being due to the high electro negativity of the Fluorine[5].

The first band at lowest I.P. (i.e. highest orbital energy), is assigned to the 2e halogen lone-pair orbital, being relatively strong and sharp as in the carbon compounds. Spin-orbit coupling occurs and increases with increasing atomic weight of halide, the splitting being of the same order as in the carbon compounds. The $3a_1$ and 2e bonding levels in the methyl halides are well separated, but in silyl and germyl chloride only one band is found and assigned to a coincidence of both levels, this band separating into the two components in the bromide and iodide. The second of these two bands becomes broader to high I.P., this being notable in silyl iodide where two maxima occur, this being a result of Jahn-Teller distortions of the ion; i.e. the removal of the degeneracy in the electronic state by vibrations, excited during ionisation, causing a change in molecular geometry. Thus the band with highest I.P. is assigned to the σ Si - H 1e bonding level and that at lower I.P. to the Si - X σ $3a_1$ level. As expected, the $2a_1$ bonding orbital is assigned to the weak band at high I.P., being consistent with an Mns orbital[4]. The weakness is due to the low sensitivity of the instrument and to the low cross-sections of s orbital electrons. Vibrational structure was found on all three bands in silyl chloride, and the first band in germyl chloride. The 2e band

TABLE III

Vertical ionisation potentials for MH_3X (eV)

(M = C, Si, Ge, X = F, Cl, Br, I). I.P. ± 0.02 eV or ± 0.1 eV

	X =	Cl			Br			I		
level	M =	C	Si	Ge	C	Si	Ge	C	Si	Ge
2e		11.28	11.61	11.30	10.53	10.96	10.61	9.54	9.78	9.59
					10.84	11.10	10.83	10.16	10.33	10.14
$3a_1$		14.4	13.4	13.05	1.35	12.85	12.51	12.5	12.04	11.71
1e		15.5	13.7	13.3	15.1	13.3	12.9	13.8	12.8	12.6
$2a_1$		–	18.04	18.52	–	18.1	18.33	–	–	–
$1a_1$		–	–	–	–	19.5	19.20	–	–	–

TABLE IV

Vertical Ionisation Potentials for MH_2X_2 (eV)

(M = C, Si, Ge, X = F, Cl, Br, I). I.P. ± 0.02 eV or ± 0.1 eV

X =	Cl			Br			I		
level M =	C	Si	Ge	C	Si	Ge	C	Si	Ge
$4a_1$	11.4	11.64	11.42	10.63	10.92	10.69	9.52	9.69	9.56
$1a_2$	11.5	12.06	11.72	10.83	11.12	10.85	9.83	9.99	9.82
$2b_1$	12.2	12.50	12.08	11.25	11.61	11.28	10.29	10.35	10.18
$2b_2$							10.63	10.73	10.53
$1b_2$	15.1	14.3	13.76	14.0	13.35	12.93	12.9	12.13	11.89
$3a_1$	15.8	-	-	14.6	-	13.17	13.8	12.63	12.32
$1b_1$	16.6	-	-	16.0	13.7	13.71	15.8	13.24	13.02
$2a_1$	-	18.12	-	-	-	-	-	-	-

shows a progression in 520 ± 40 cm^{-1} for silicon and ~ 400 cm^{-1} for germanium, these being assigned to reduced M – Cl stretching frequencies, (ground state frequencies 551 and 423 cm^{-1} respectively). The progressions could be assigned to reduced MH_3 rocking modes but the selection rule that only symmetric vibrations can be excited makes this less likely. The second band in silyl chloride shows a progression of six members with a spacing of 480 ± 40 cm^{-1} assigned to a reduced Si – Cl stretching vibration, this being consistent with the assignment of the band to the $3a_1$ Si – Cl σ bonding level. The third band shows a progression of 1760 cm^{-1} similar to that in silane[4] being assigned to a reduced Si – H stretching frequency and is thus in agreement with the assignment to the $2a_1$ Si – H bonding level.

On comparing the I.P.s with those of the carbon compounds, the first I.P.s are seen to change in the order Si > C ≃ Ge. On the basis of the different I.P.s of the p orbitals of the Group IV elements, C > Si ≃ Ge[7], the I.P.s of molecular orbitals involving the Group IV atom p orbitals would be expected to follow this change, as is found for the $2a_1$, $3a_1$ and 1e levels. Similarly non-bonded electrons would be expected to change I.P. in a similar fashion due to the differing electro-negativities of the Group IV atoms, C > Si ≃ Ge. The greater I.P. for silicon than carbon is most easily explained in terms of (p → d) π bonding between the halogen lone-pair electrons and the silicon 3d orbitals. The band shape and the excited vibrational progression of the 2e band, which indicates that the lone-pair is not completely non-bonding as in methyl chloride, is further evidence of this. The effect appears to decrease as the halogen changes from chlorine to iodine as concluded from U.V. spectra[2].

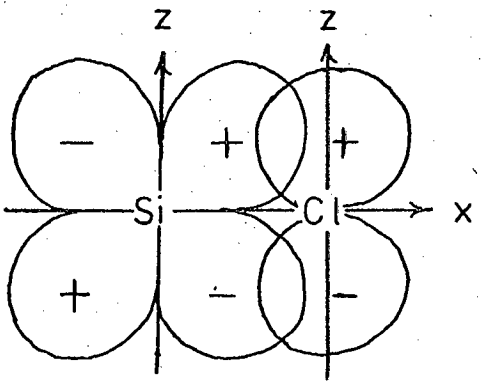

Fig I

Si $3d_{xz}$ + Cl p_z orbitals

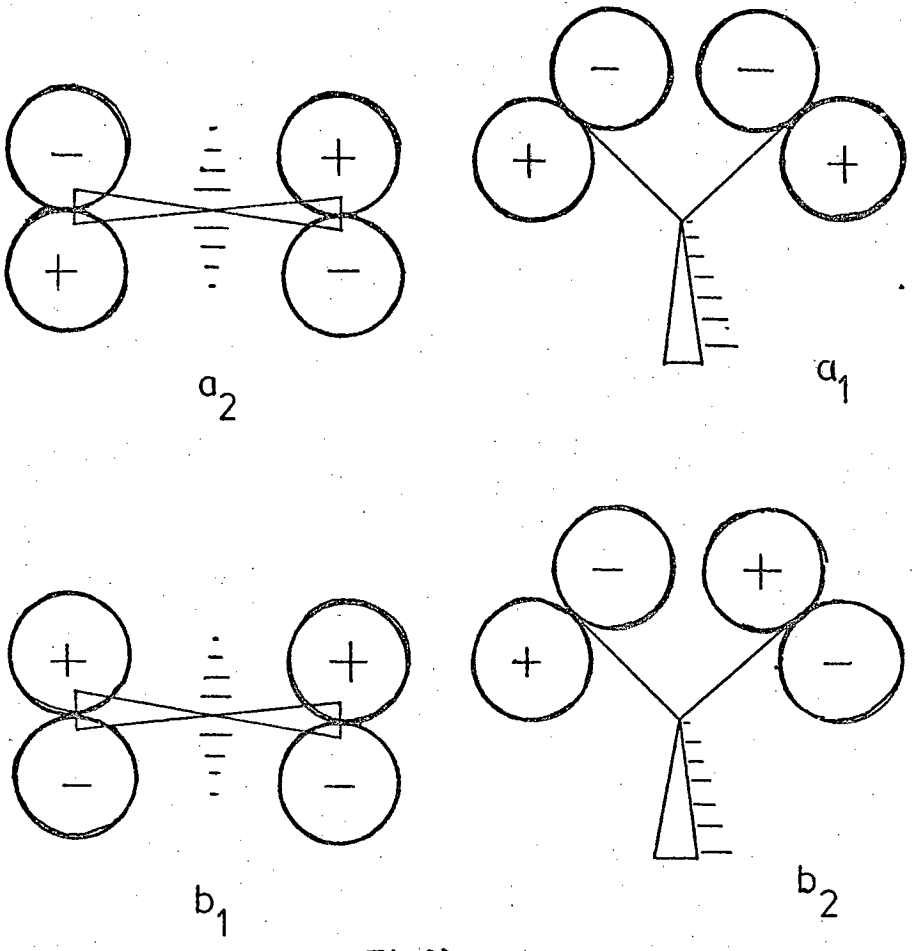

Fig II

Combinations of Xp_π lone-pair orbitals in MH_2X_2

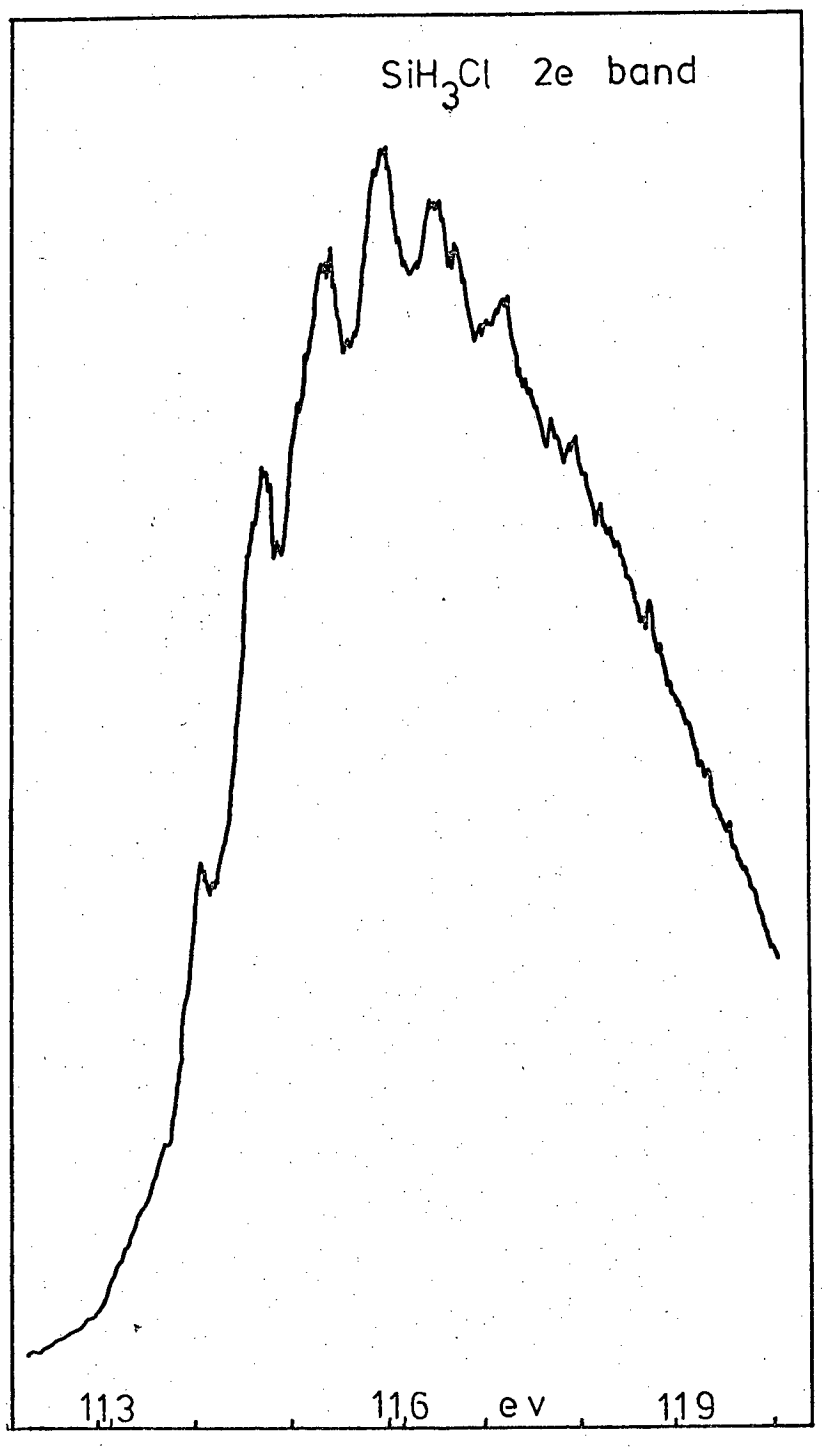

Fig Ia

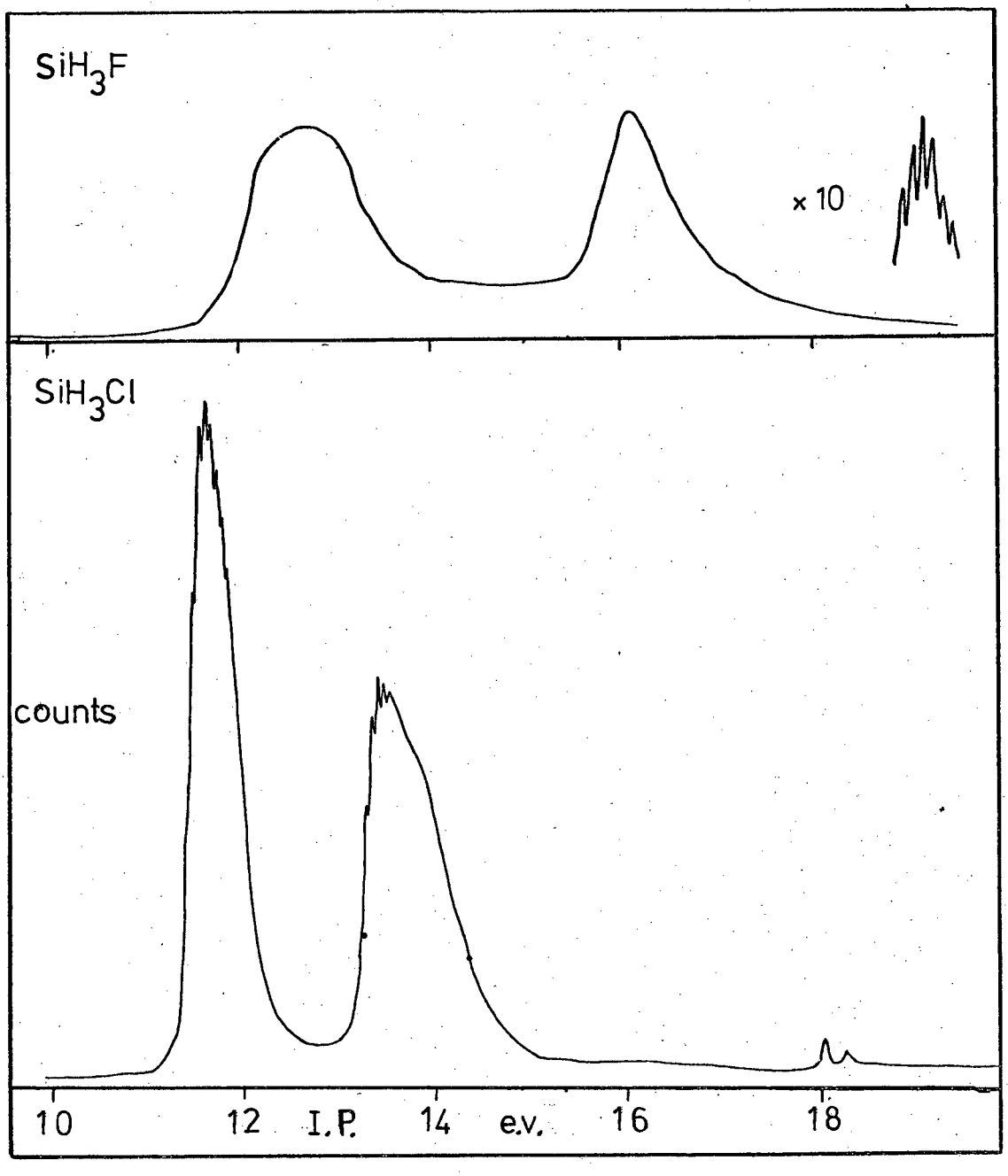

Fig III

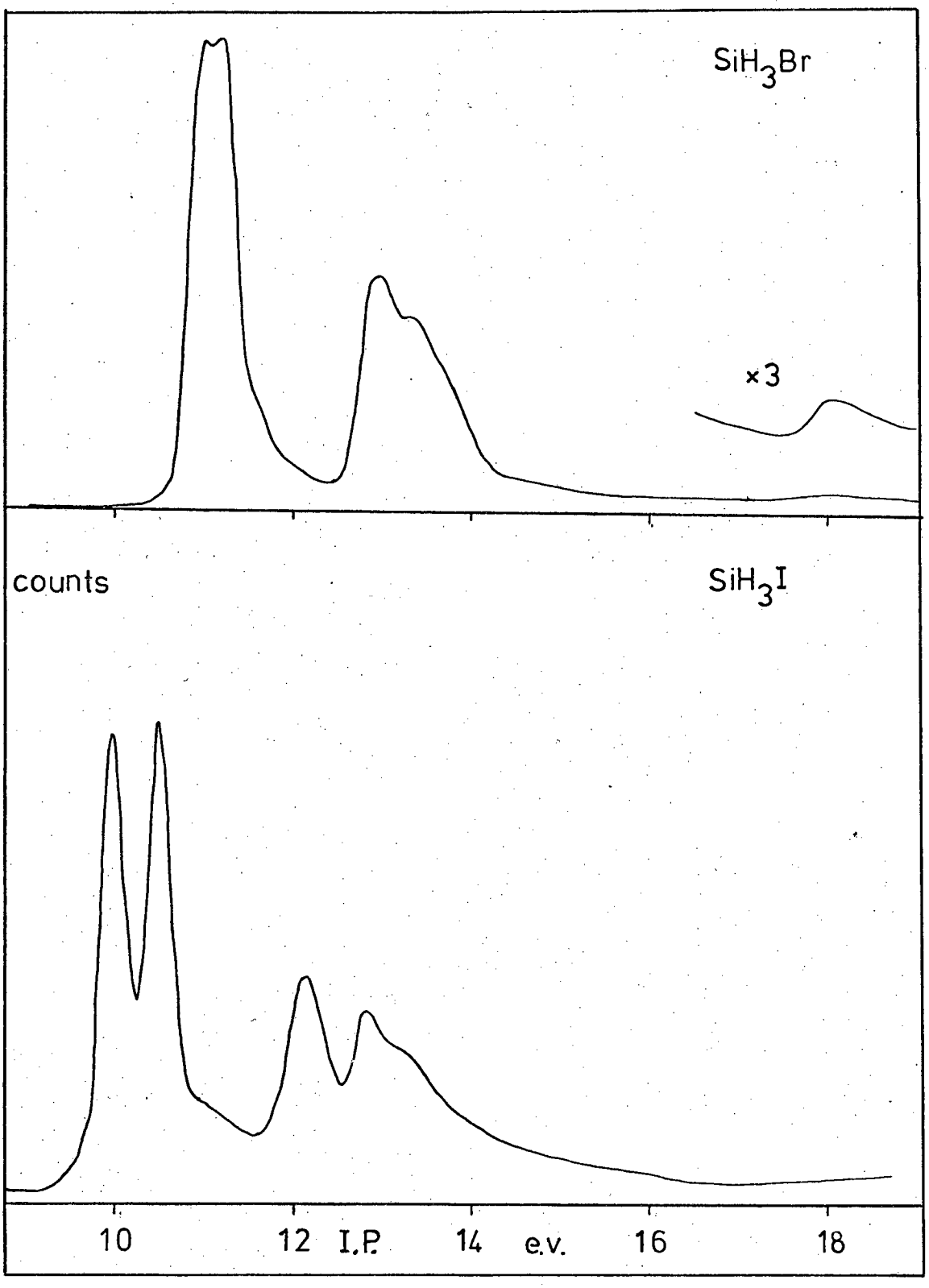

Fig IV

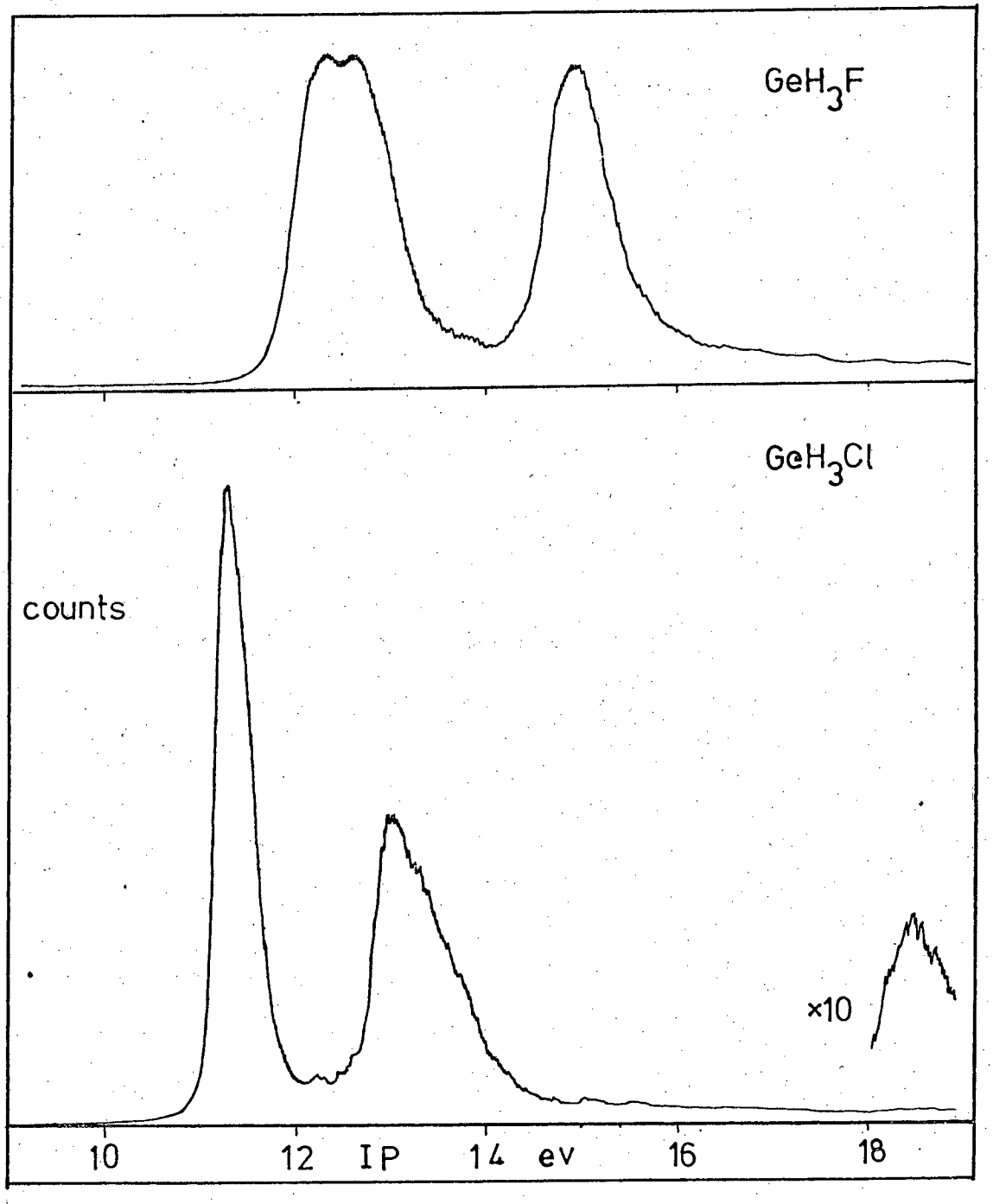

Fig V

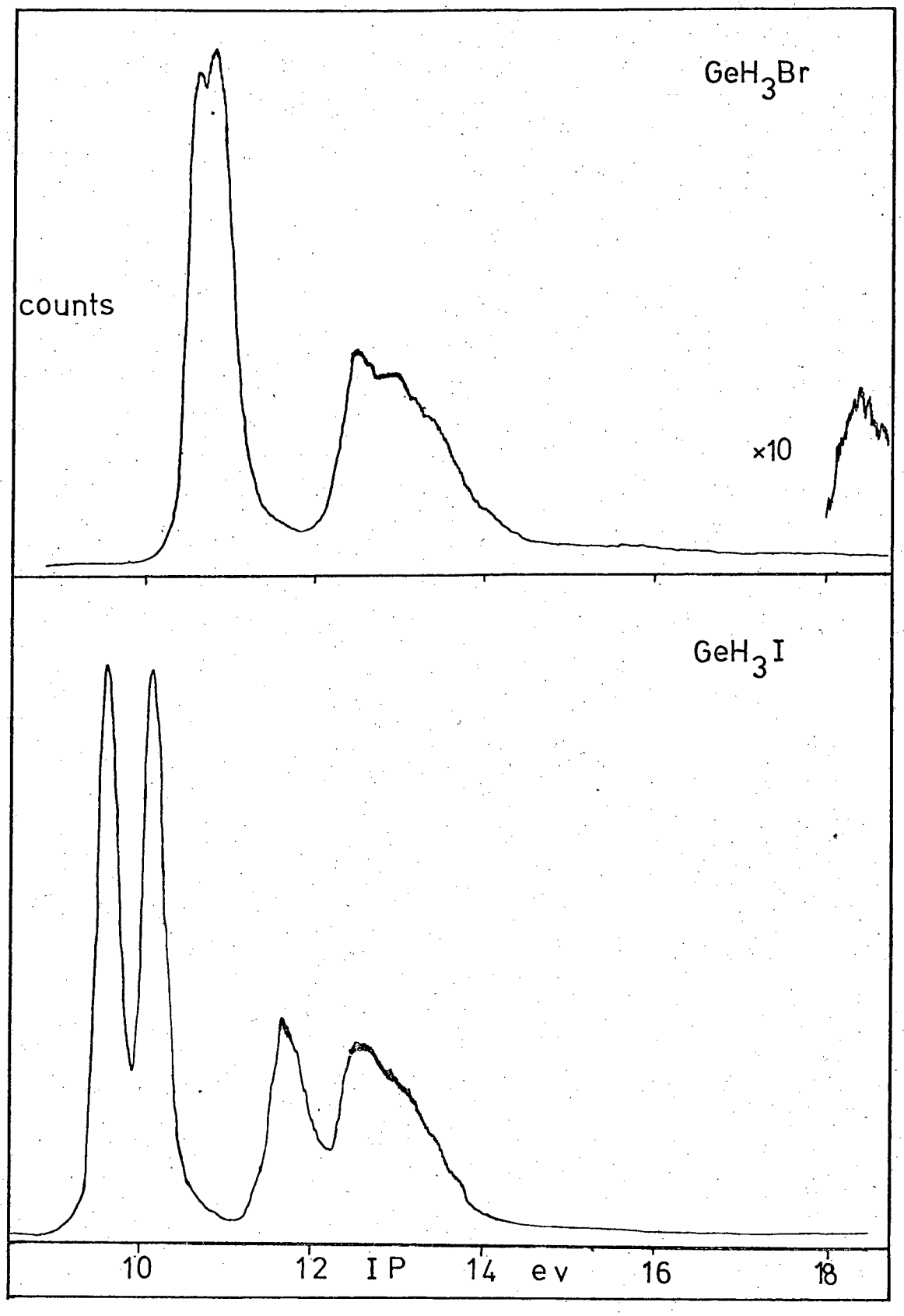

Fig VI

The Spectra of the dihalides are more complex, the fluorides again being considered separately. The sharp bands at high I.P. are assigned to the four lone-pair orbitals. The four levels are resolved in the iodides but in the chlorides and bromides, two must be coincident. The second band is assigned to the $3a_1$ and $2b_2$ M - X and $1b_1$ M - H bonding levels, again being resolved in the di-iodides but coincident in the chlorides. A third band in dichlorosilane at high I.P. is assigned to the Si 3s level as in silyl chloride. An interesting point is the ordering of the levels. Comparison with the spectra of the methylene halides[6] and the mono-halosilanes leads to an assignment of the σ levels in the order $2b_2 < 3a_1 < 1b_1$, i.e. the M - X level at highest energy and the M - H at lowest energy. For the lone-pair levels, a number of factors must be considered. The orbitals are considered as perpendicular to the M - X σ bonds and so the relative energies due to maximum overlap of the orbitals will be $a_2 > b_2 > b_1 > a_1$, more overlap giving greater stability. Interaction with other levels of the same symmetry, disturbing this ordering, can occur in two ways. Interaction with the $3a_1$ and $2b_2$ M - X and $1b_1$ M - H σ levels will tend to destabilise lone-pair levels of a_1, b_1 and b_2 species with respect to the a_2 level. Interaction with the d orbitals on M, which transform as 2 x a_1, a_2, b_1 and b_2 will tend to stabilise all the lone-pair levels, possible the a_1 to a greater extent. As these two effects are opposite and in no way related, the relative ordering must be a matter for conjecture. Calculations on the methylene halides including both the C - X and X - X interactions lead to an assignment $b_2 > b_1 > a_2 > a_1$[12], and similar calculations on dichlorosilane including d orbitals given the same ordering and very good agreement with

experimental values, (13). On comparing the I.P.s to those of the methylene halides, the trend in I.P. Si > C ≃ Ge is again found suggesting (p → d) π bonding.

Consider the fluorides, table (V), (the 1e and 2e levels changing character). None of the bands are found to be sharp as in the other halides, this being similar to the carbon compounds and a general feature of the P. E. spectra of fluorine containing compounds, (see chapter VI and e.g. 8, 10 and 11). In the monofluorides as in the methyl compound, there are fewer bands than expected, implying coincidence of several of the energy levels, as predicted from calculated energies[9,13]. The first band is assigned to the 1e level, being mainly M - H σ bonding. Silyl fluoride shows no Jahn-Teller splitting of this level whereas in germyl fluoride it is about 0.4 ev, the same as in methyl fluoride[8]. The second band, by analogy with SiF_4[10], and GeF_4[11], is assigned to both the $3a_1$ Si - F σ and 2e fluorine lone-pair levels. Comparison of the 1e and 2e levels of the fluorides and chlorides shows that σ/π interaction could be large, although electro-negativity must be taken into account. However, the low value of the 1e level shows an apposite trend from the perfluoro-effect [14,15]; that fluorine usually stabilises σ levels. The Si 3s $2a_1$ level is again found at high I.P. with an excited progression of frequency 810 ± 40 cm^{-1}. Assignment to an Si - F stretching or Si - H bending vibration is possible, both being of a_1 symmetry, (νSi - F = 890 cm^{-1}, δSiH_3 = 990 cm^{-1}). Computed energy levels[9] indicate considerable Si - F σ bonding character, which would lead to excitation of the Si - F stretch. There is a shift to higher I.P. of 0.3 eV from the chloride and bromide, due to the large electro-negativity of the fluorine. The

TABLE V

Vertical Ionisation Potentials, (eV) for

(a) MH_3F and (b) MH_2F_2. (M = C, Si, Ge). I.P. $\pm$ 0.1 eV

(a)

level	M = C	Si	Ge
2e	13.1	12.6	12.3
$3a_1$	17.	16	15
1e	17.1	16.2	15.0
$2a_1$	-	19.27	-

(b)

level	M = C	Si	Ge
$2b_1$	13.3	12.9	13.0
bonding and $F2p_\pi$ levels	15.3	15.2	14.6
	15.7	16.0	16.3
	18.9	17.9	

lowest band in the difluorides is again in each case assigned to the $1b_1$ σ M – H orbital as in difluoromethane[8]. The next two bands in the silane are assigned to fluorine lone-pairs, by comparison to SiF_4, these levels coinciding in difluorogermane at 14.6 eV, the splitting in the silane being a result of $(p \rightarrow d)\pi$ bonding. The last band is assigned to the $2a_1$ M – F σ bonds. The diffuseness of the bands implies σ/π mixing, this being suggested by calculations[13].

Thus it would appear that they type of bonding is as suggested by sp^3 hybridisation, but there is additional π bonding from the halogen lone-pairs, and the s orbitals are not involved 100%.

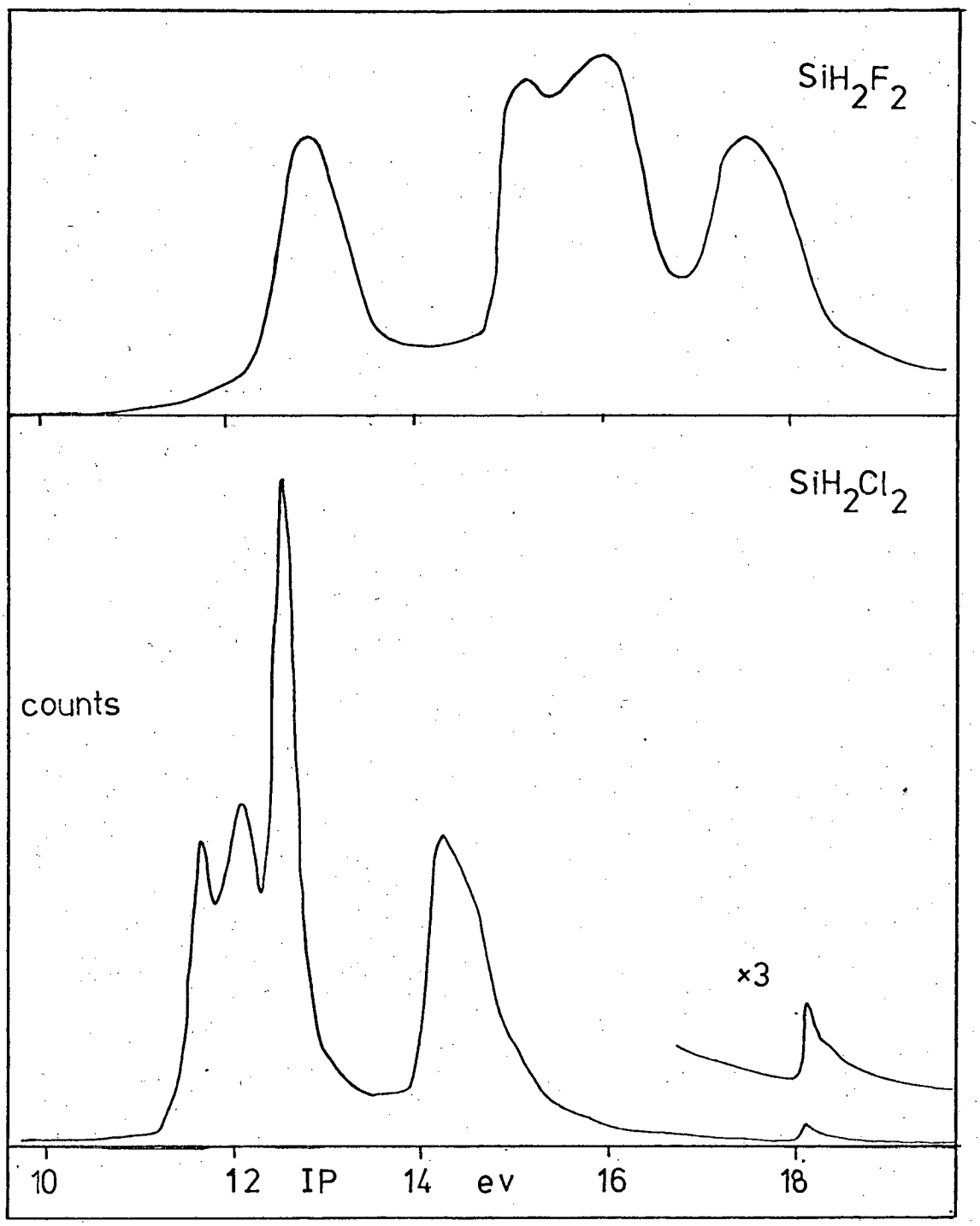

Fig VII

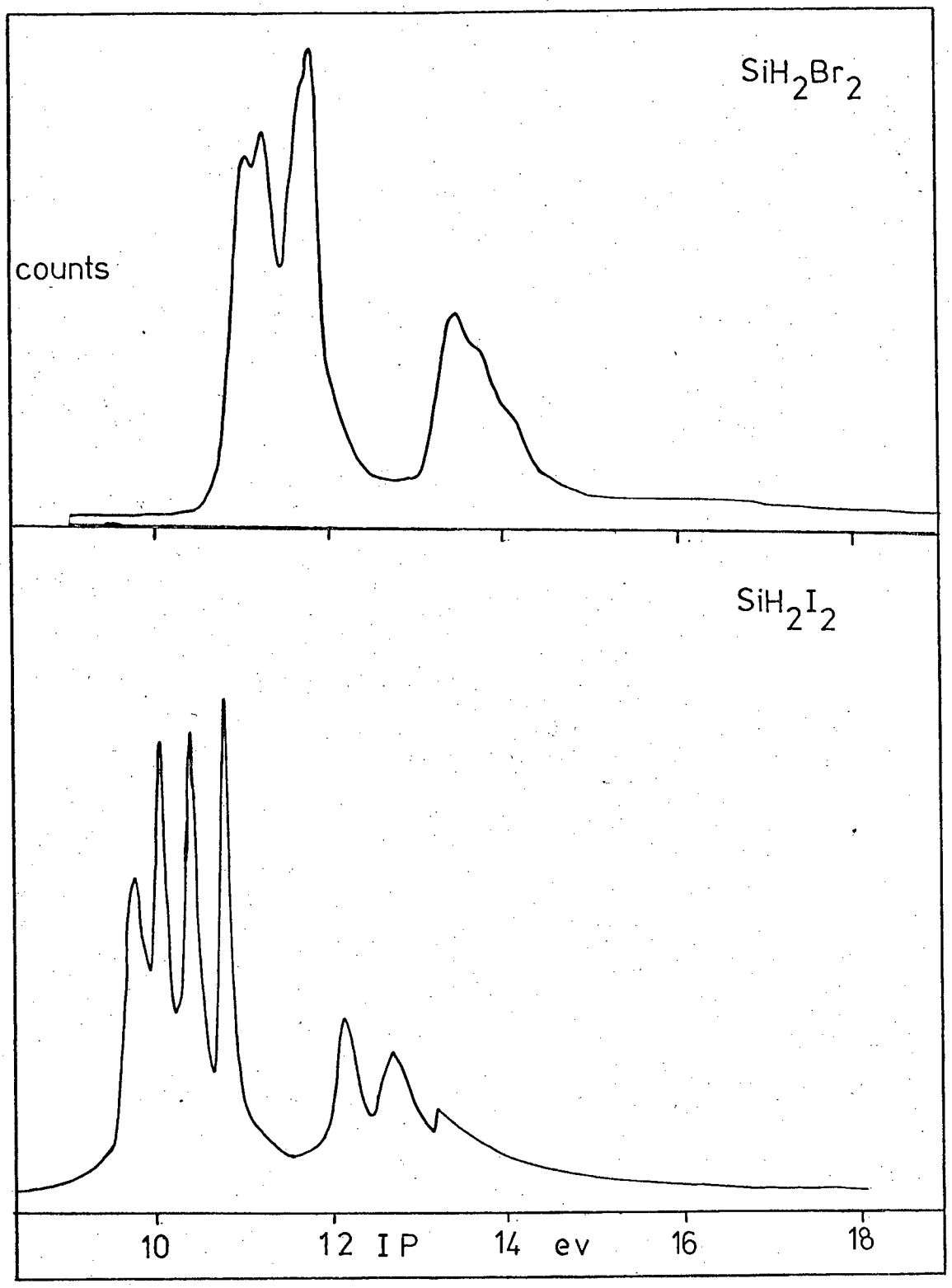

Fig VIII

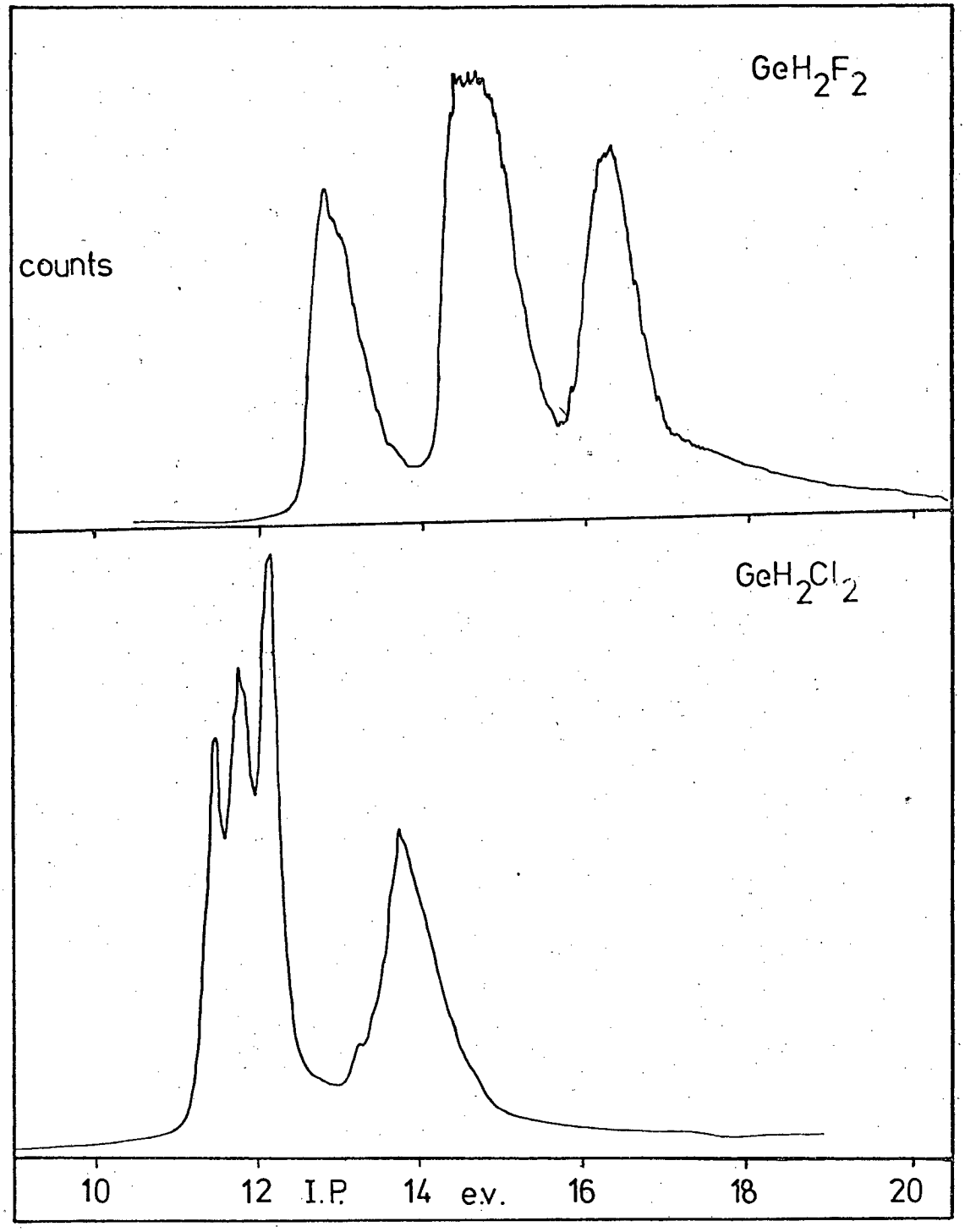

Fig IX

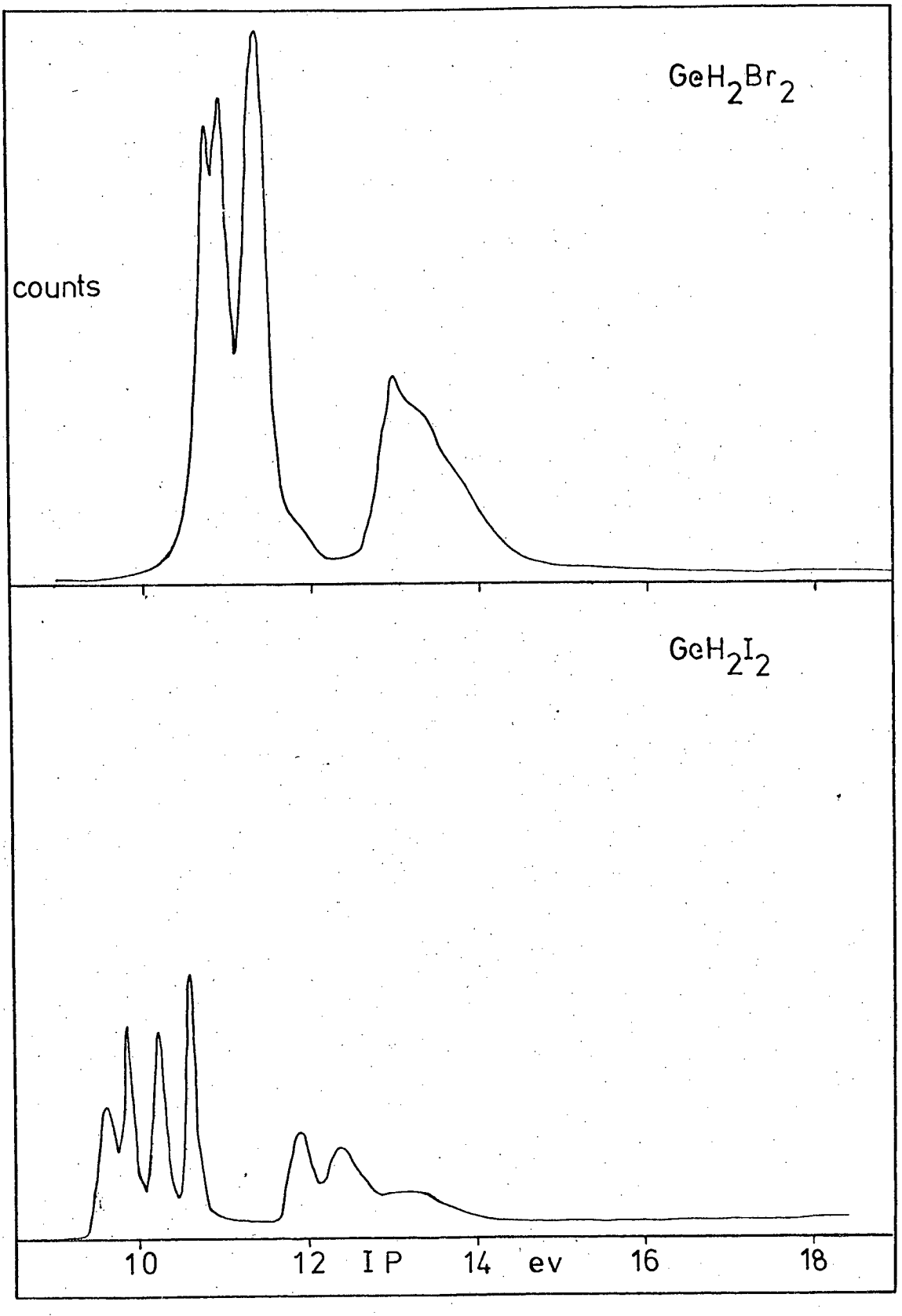

Fig X

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CHAPTER TWO

The Photo-electron Spectra of some silyl and germyl Derivatives of the Group IV Elements

Introduction

The derivatives of the group Iv elements, O, S, Se and Te, have an interesting skeletal electronic structure because of the possibility of $(p \rightarrow d)\pi$ bonding from the group VI atom lone-pair electrons to the group IV atom d orbitals in the molecules $MH_3 - Y - MH_3$, (Y = O, S, Se, Te) and MH_3SH, (M = Si, Ge).

The chemistry of disilyl sulphide and disilyl selenide is interesting on comparison to their carbon analogues. They do not react with methyl iodide, silyl iodide, or boron trichloride to give adducts, and they do not form sulphonium or selonium salts with iodine, as does diethyl sulphide[2]. All these reactions indicate that the lone-pair electrons are more strongly held, which is the opposite to that expected from consideration of the high electro-positivity of silicon, but is good evidence for $(p \rightarrow d)\pi$ bonding. The short bond lengths and large M - O - M bond angles from electron diffraction structure determinations of disiloxane and digermoxane[3,4] have been interpreted in terms of such bonding; a widening angle implies an increase in lone-pair p character and hence overlap with the π type d orbitals will be at a maximum, σ bonding from oxygen occurs via sp hybrids. Similar conclusions have been drawn from their infra-red spectral band shapes[5,6]. However, the ultra-violet spectrum of disiloxane shows a shift to lower energy of about 1.5 eV from dimethylether. This can be interpreted in terms of $(p \rightarrow d)\pi$ interaction or by d orbital interaction with the lowest anti-bonding orbital, this being more favourable energetically[7]. Conversely, the electron diffraction structure determinations of disilyl and digermyl sulphide[8,4] amd disilyl and digermyl selenide[9,4] indicate normal M - Z bond lengths and bond angles at Y of

about 95°, however, the lack of linearity does not necessarily preclude π bonding.

Of the thio-acids, SiH_3SH and GeH_3SH, little is know due to their instability in the gas phase. They undergo a disproportionation reaction to give the corresponding sulphides and hydrogen sulphide, which results in an equilibrium mixture. The equilibrium is slow in being reached for silyl mercaptan, allowing its characterisation[1]. Silyl mercaptan readily forms anions, it smmonium [10] and lithium salts[11] being stable at room temperature. Si d orbital interaction could again be a stabilising influence in the anion formation.

Another factor in the bonding of these compounds is the inclusion in the general molecular orbital scheme, of the d orbitals of the group VI atom. d orbital participation has been shown to occur in sulphur compounds with π-donor substituents. Calculations of the orbital energies of SO_2F_2 to include d orbitals give good agreement with experimental I.P.s[12] and an orbital correlation diagram with SO_2Cl_2 indicates mixing between the Op_π and Fp_π levels via the S 3d π orbitals[13]. Recently the spectrum of SO_3 has been interpreted by invoking S 3d orbitals in the molecular bonding [14]. However, the likely interaction of S 3d orbitals with benzene π orbitals in thiophenol has been shown to be small[15]. As there are no π orbitals in the MH_3 groups to donate to the S 3d orbitals, they have been ignored.

Spectra and Assignments

The spectra of the compounds $(MH_3)_2Y$, (M = Si, Ge; Y = O, S, Se, Te) and MH_3SH, (M = Si, Ge) are shown in Figures (I to V) and the vertical ionisation potentials are listed in tables I and II together with those of the carbon analogues for comparison[16]. The group (VI) compounds are

TABLE I

Vertical Ionisation Potentials of $(MH_3)_2Y$, ($\pm$ 0.02 eV),

(M = C, Si, Ge, Y = O, S, Se, Te)

M	Z	$2b_1$ p_x	MH	$4a_1$	$3b_2$	Mns
C	O	10.04	14.2 16.5	11.91	13.42	-
Si	O	11.17	12.5	11.2	14.5	17.2
Ge	O	10.40	12.2	10.9	13.4	-
C	S	8.71	14.5	11.28	12.68	-
Si	S	9.70	12.5	11.15	11.71	16.9
Ge	S	9.25	12.3	10.66	11.30	-
C	Se	8.40	14.0	11.0	12.0	-
Si	Se	9.18	12.5	10.85	11.29	16.75
Ge	Se	8.84	12.2	10.44	10.88	-
C	Te	7.89	15.0	10.35	11.32	-
Si	Te	8.63	12.3	10.23	10.83	-
Ge	Te	8.34	12.2	9.93	10.56	-

TABLE II

Vertical Ionisation potentials of MH_3SH. ($\pm$ 0.02 eV),

(M = C, Si, Ge)

M	S 3p	MH	MS	SH
C	9.44	15.1	12.0	13.7
Si	9.97	12.5	11.75	14.41
Ge	9.69	12.5	11.39	14.08

assumed to have C_{2v} symmetry, the z axis lying along the two-fold axis of rotation and the M - Y - M skeleton lying in the yz plane. The valence shell atomic orbitals and molecular orbitals are shown in tables III and IV respectively. The molecular orbitals have been derived assuming only interaction between atomic orbitals of identical symmetry and similar energy. There will also be unfilled anti-bonding combinations corresponding to the bonding ones. The ns orbitals of M and the n's orbitals of Y are considered as retaining their character as in the halides. The n's levels probably lie beyond the range of the machine, the values for water and hydrogen sulphide being 32 and 22 eV respectively[17]. Even with inductive raising of the energy by the silyl or germyl groups from these values, their low-cross-section makes detection difficult. The p orbtials on the group IV atoms have been divided into two sets. p_π orbitals interact with the hydrogen 1s orbitals to give M - H σ bonds in all four classes, and there is also a contribution to the M - H bonding from the Mns orbitals. The p_σ orbitals interact with the group VI p_z and p_y orbitals, where most directional overlap occurs, in a_1 and b_2 combinations to form the $4a_1$ and $3b_2$ M - Y σ bonds. The Y p_x $2b_1$ orbital is thus considered as essentially non-bonding in character as is the Yn's orbital. The five d orbitals on the group IV atoms, Si and Ge, give 2 x a_1, a_2, b_1 and b_2 combinations of atomic orbitals which can intereact with any of the bonding orbitals. The twenty electrons needed to fill the ten bonding orbitals are supplied from the central atom, (6), the group IV atoms, (8), and the hydrogens, (6).

The mercaptans have C_s symmetry, the M - S - H skeleton lying in the plane of symmetry, and the molecular orbitals have only two classes,

TABLE III

Symmetry classes of the valence shell atomic orbitals of $(MH_3)_2Y$, (M = C, Si, Ge; Y = O, S, Se, Te)

	a_1	a_2	b_2	b_1
Yn's	/			
Yn'p_z	/			
Yn'p_y			/	
Yn'p_x				/
Mns	/		/	
Mnp_σ	/		/	
Mnp_π /Hls	///	//	///	//
Mnd	///	//	///	//

TABLE IV

Symmetry classes of the molecular orbitals of $(MH_3)_2Y$

	a_1	a_2	b_2	b_1
Ynp_x				$2b_1$
M - Y σ bonding	$4a_1$		$3b_2$	
M - H σ bonding	$3a_1$	$1a_2$	$2b_2$	$1b_1$
Mns (M - H bonding)	$2a_1$		$1b_2$	
Yn's	$1a_1$			

a' and a". The constituent valence shell atomic orbitals and the molecular orbitals derived from them are shown in tables V and VI. Again s orbitals are assumed to retain their character and the Mnd orbitals, which occur in both classes, can combine with all classes. The M - S, M - H and S - H σ levels are all in the a' symmetry class. As for $(MH_3)_2S$ the sulphur 3p lone-pair, here in the a" class, is alone in its symmetry class except for the M - H σ and Mnd levels.

The spectra of $(MH_3)_2$ Y are very similar, (Y = S, Se, Te), as are those of MH_3SH. Considering $(MH_3)_2Y$, the first band in each case, at low I.P. representing high orbital energy, is narrow, intense and structureless, characteristic of lone-pair electron ionisation and is thus assigned to the $2b_1$ lone-pair electrons as in the parent hydride[18], where it occurs at 10.47, 9.88 and 9.14 eV in H_2S, H_2Se and H_2Te respectively, the reduction being a result of the inductive effect of the MH_3 group. The next two bands at higher I.P. occuring between 10 and 12 eV are of equal intensity. They both decrease in I.P. on changing from sulphur to selenium to tellurium for a given M, the decrease reflecting the change in electro-negativity difference, and the difference between them is greatest for S and least for Se as for the hydrides. They are thus assigned to the $4a_1$ and $3b_2$ M - Y bonding levels, the $4a_1$ being at lower I.P. and the more anti-bonding $3b_2$ at higher I.P. as in the hydrides. These could be assigned in the reverse order on the grounds that less overlap of orbitals in the b_2 combination will produce a less stable level than the a_1. However, the a_1 could be destabilised by interaction with other a_1 levels, there being more of such interactions possible than with the b_2 levels. The band between 12 and 14 eV for Si and 11 and 13 eV for germanium has been assigned to the M - H σ levels

TABLE V

Symmetry classes of (a) valence-shell atomic orbitals, (b) molecular orbitals of MH_3SH, (M = C, Si, Ge)

(a)

a'	a"
Si 3s	
Si $3p_z$	Si $3p_y$
Si $3p_x$	
2H 1s	H 1s
S 3s	
S $3p_z$	S $3p_y$
S $3p_x$	
H 1s	

(b)

M – H, S – H, M – H, M – S	anti-bonding	9a'	M – S, M – H, S – H	bonding	5a'
		8a'			4a'
		7a'			3a'
		6a'	M – H (Mns)		2a'
			S 3s		1a'

M – H anti-bonding	3a"
S $3p_y$ lone-pair	2a"
M – H bonding	1a"

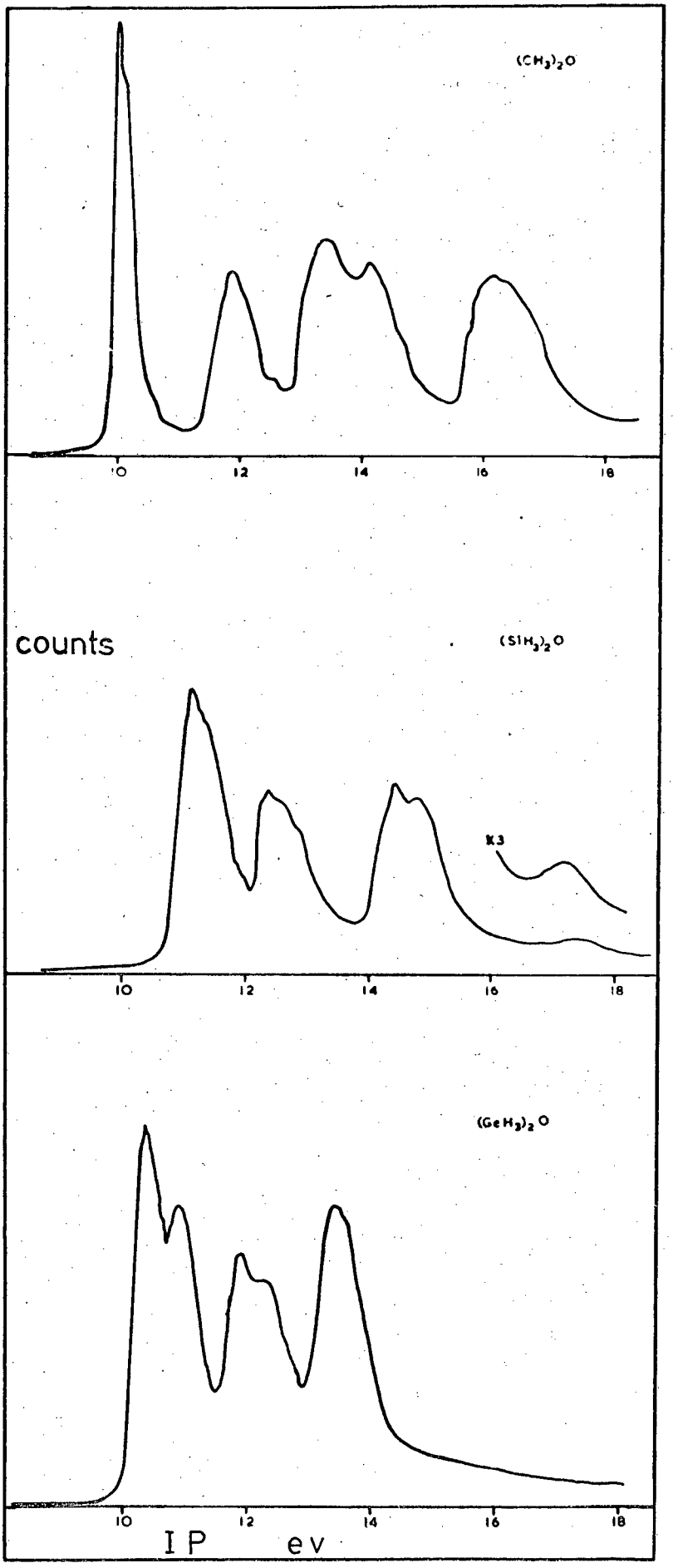

$(CH_3)_2O$
10
12
14
16
18
counts
$(SiH_3)_2O$
X3
10
12
14
16
18
$(GeH_3)_2O$
10
12
14
16
18
IP ev

Fig I

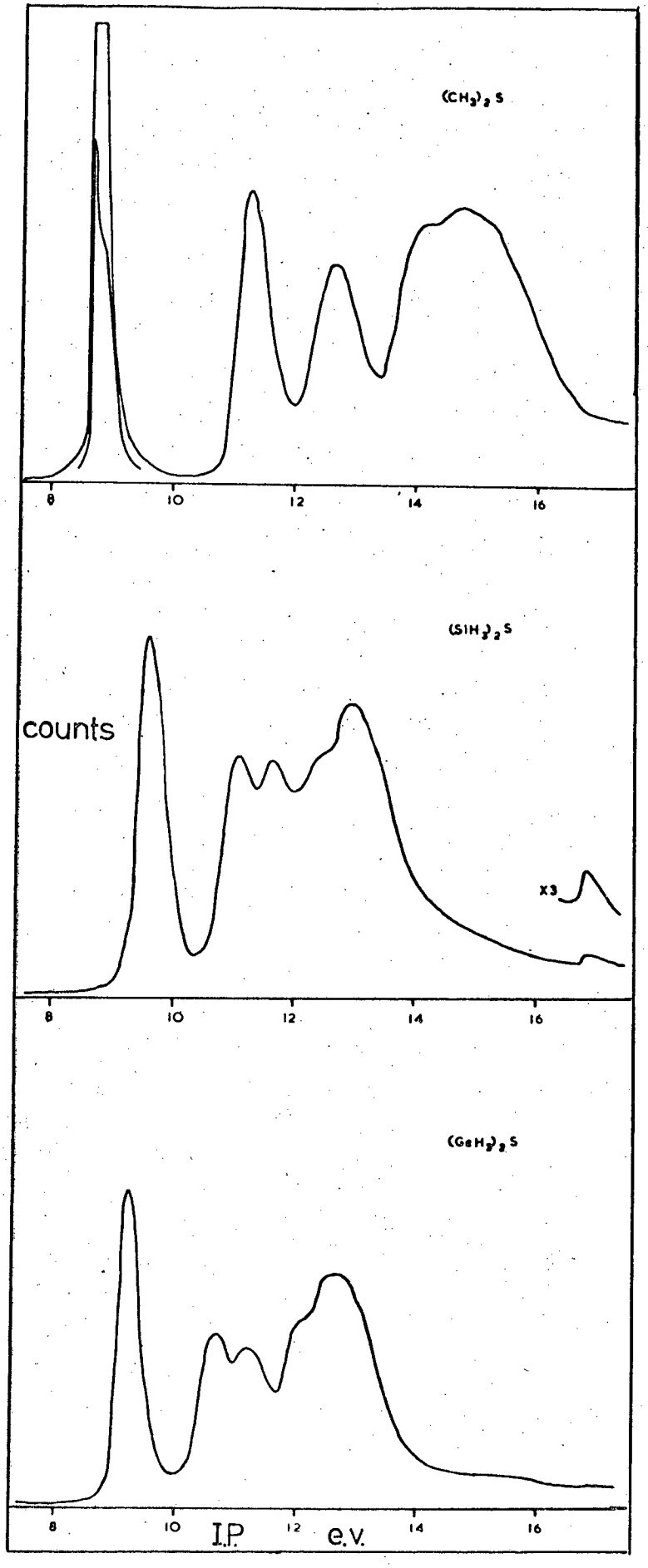
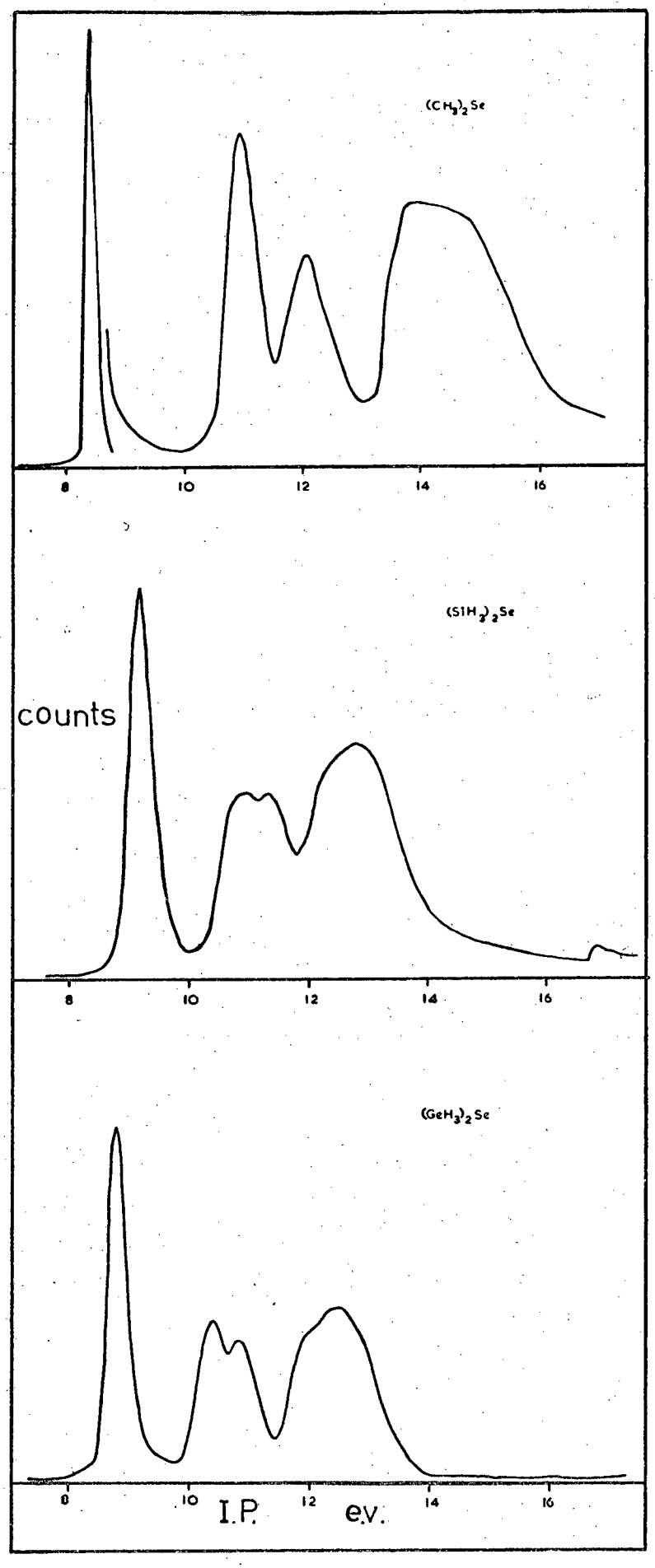

$(CH_3)_2S$
8
10
12
14
16
$(SiH_3)_2S$
counts
x3
8
10
12
14
16
$(GeH_3)_2S$
8
10
I.P
12
e.v.
14
16

Fig II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8
10
12
14
16
$(SiH_3)_2Se$
counts
8
10
12
14
16
$(GeH_3)_2Se$
8
10
I.P.
12
e.v.
14
16

Fig III

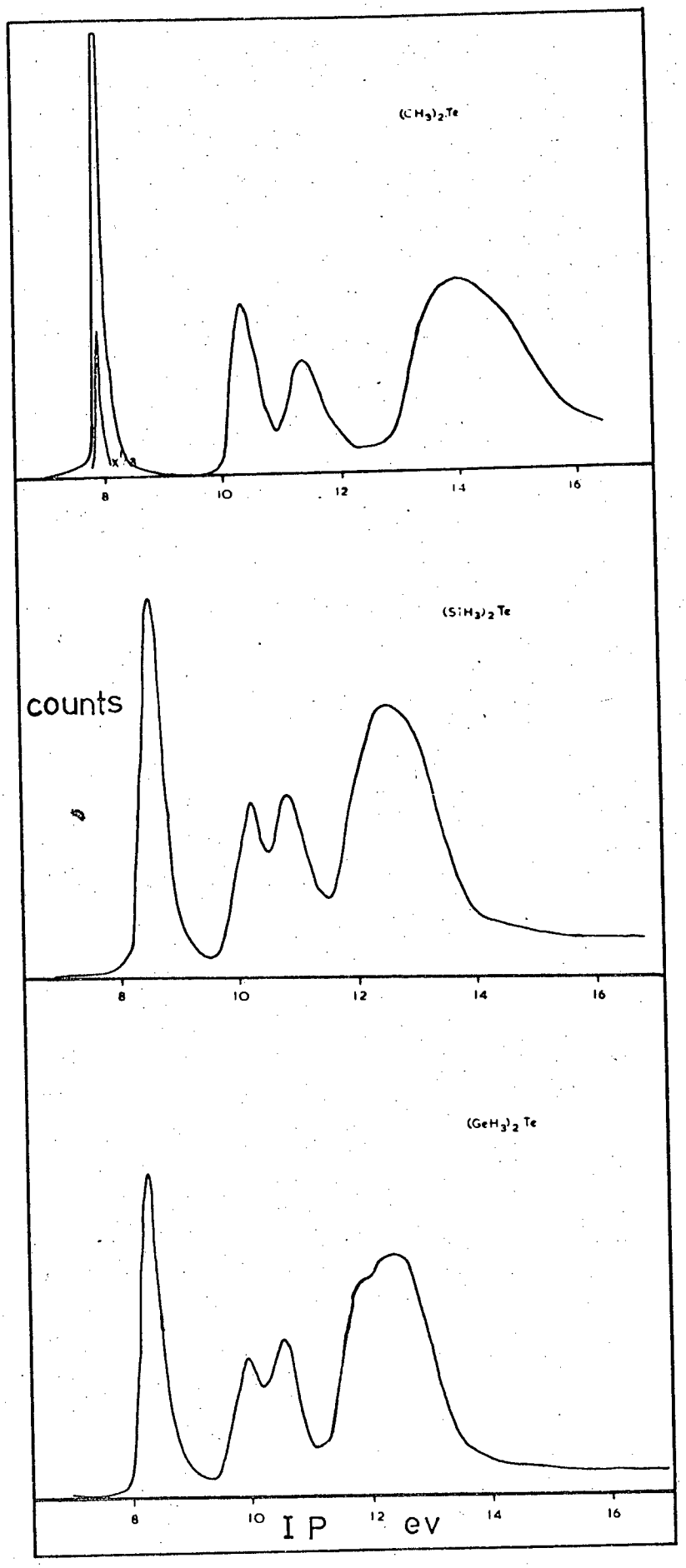

Fig IV

as in the halides, the reduction in I.P.s as M changes from C to Ge reflecting the change in electro-negativity of M, C > Si ≃ Ge. None of these bands is resolved into its four components although the germyl compounds show two slight maxima. Thus it would appear that there is little mixing between the M - H and M - Y σ levels. The relative intensity of this band to the $4a_1$ and $2b_2$ bands is 2:1 in all cases, as expected assuming localisation of the s electrons. The weak bands found at 16.9 and 16.75 eV in desilyl sulphide and selenide respectively are assigned to the symmetric and anti-symmetric combinations of the Si 3s levels, the weakness reflecting their low cross-section of ionisation. These occur at lower I.P. than in the halides ($\sim$ 18.0 eV), indicating less bonding character. This could be a result of the lower electro-negativity of sulphur and selenium but the lowering is much greater when compared to the change from silyl fluoride to sily bromide, (0.5 eV), where the electronegativity difference is greater.

Comparison of the silyl and germyl compounds to the methyl ones shows that the relative ordering for the lone-pair ionisation potentials is again Si > C ≃ Ge, as for the halides, this being opposite to that expected from electronegativity changes. The only orbital available to stabilise the $2b_1$ lone-pair orbital is the Mnd b_1 orbital since the only other possible interaction, with the $1b_1$ M - H σ level, would destabilise the $2b_1$ level.

The spectra of the mercaptans are very similar to each other and the first sharp band is again assigned to the lone-pair 2a" level. The destabilisation of the sulphur lone-pair level in silyl mercaptan from H_2S is about 0.5 eV, whereas on substitution of a second silyl group to give disilyl sulphide, the lone-pair is only destabilised by a further

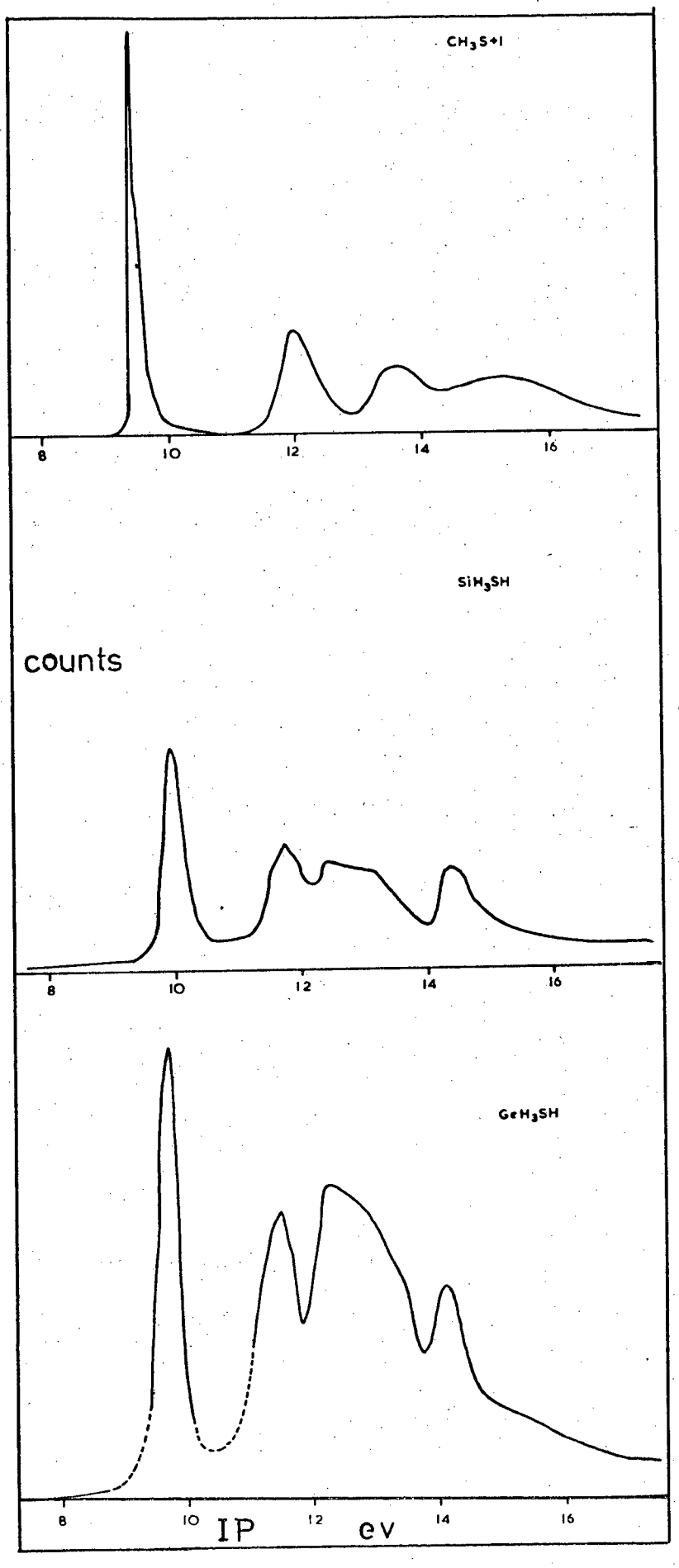
CH_3S^+I
8
10
12
14
16
SiH_3SH
counts
8
10
12
14
16
GeH_3SH
8
10
IP
12
ev
14
16

Fig V

0.25 eV. Thus it would appear that stabilisation of the lone-pair by back-bonding via d orbitals increases to a greater extent than inductive destabilisation as the number of silyl substituents increases. The second band is assigned to the 5a' M – S σ level and is very similar to the $3b_2$ level in $(MH_3)_2S$, decreasing as the electronegativity of M decreases. The 4a' and 1a" M – H levels are assigned to the third band for M = Si and Ge and to the fourth band for M = C. No splitting of the levels by orbital interaction could be detected although the peak is flat-topped and broadens to higher I.P. for the silyl and germyl compounds. Again the I.P.s decrease from C to Ge. The remaining band is assigned to the 3a' S – H bond, being of similar energy to the b_2 level in H_2S, (14.79 eV). The change in I.P. of this band is of interest. Calculations have shown the 5a' C – S σ and 3a' S – H σ levels of CH_3SH to be equally mixed and thus the raising of the 3a' level in SiH_3SH may be due to such mixing being more favourable[19]. Alternatively it could be due to the inductive effect of a silicon atom at the β position. On comparing the band shapes of $(CH_3)_2S$ and CH_3SH to the first bands in the silyl and germyl compounds, the latter show greater bonding character, being less intense and broader, with a half-width of about 0.5 eV. This, with the trend in first I.P.s is again consistent with $(p \rightarrow d)$ π bonding.

Considering the oxides, shown in Figure (I), a more complex situation occurs the spectra being markedly different, not only from each other but from the compounds of the other group VI elements. This is not surprising in view of the almost linear nature of disiloxane which will give the molecule approximatic D_{3h} symmetry. If the z axis is again considered as lying along the C_2 axis and the y axis along the

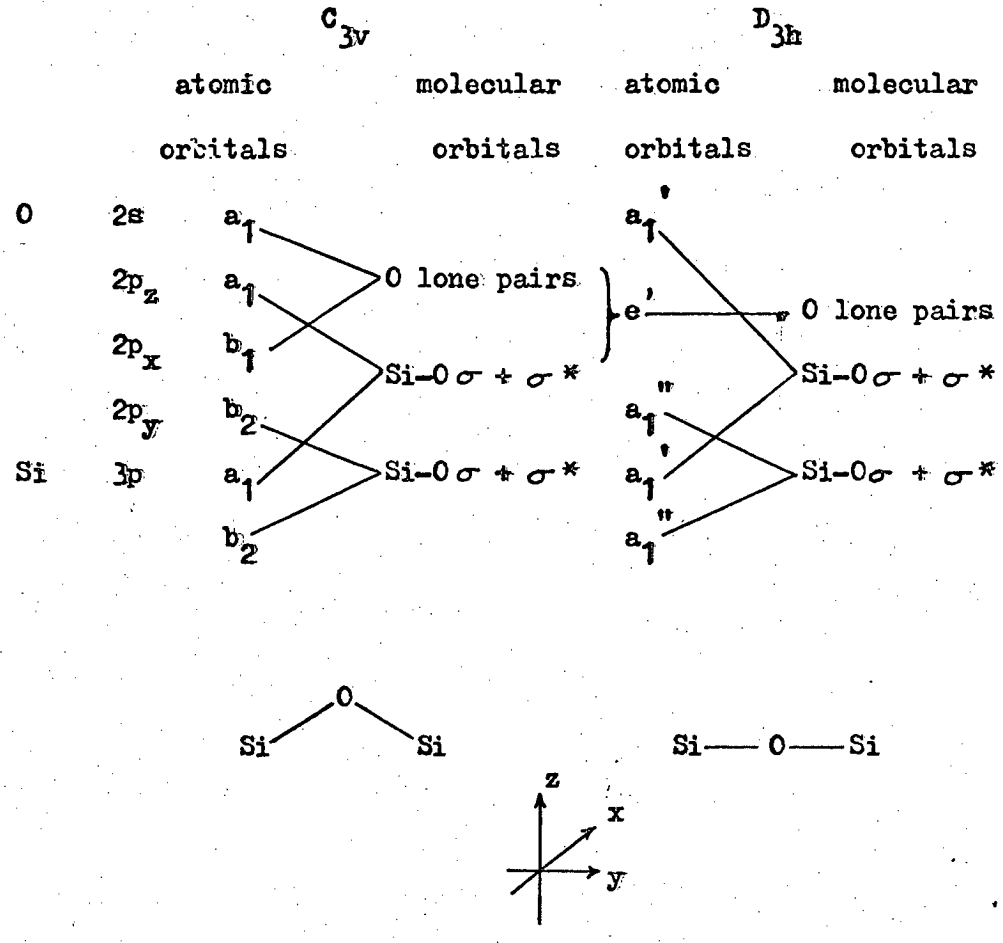
C3v
D3h
atomic orbitals
molecular orbitals
atomic orbitals
molecular orbitals
O
2s
2pz
2px
2py
Si
3p
a1
a1
b1
b2
a1
b2
0 lone pairs
Si-O σ + σ*
Si-O σ + σ*
a1'
e'
a1''
a1'
a1''
0 lone pairs
Si-O σ + σ*
Si-O σ + σ*
Si
O
Si
Si — O — Si
z
x
y

Fig VI

Si - O bond, the horizontal plane of symmetry will be in the xz plane. Considering the atomic orbitals, the p_z and p_x orbitals of oxygen will transform as a doubly degenerate e' level while the p_y changes class from b_2 to a_2''. Similarly the Si $3p\sigma$ levels, now directed along the molecular axis now belong to a_1' and a_2'' classes and the oxygen 2s stays in the totally symmetric a_1' class. The skeletal molecular orbitals can now only be constituted in one way as shown in Figure (VI) because of the doubly-degenerate lone-pair level; the Si - O σ bonding and anti-bonding levels now being constituted from O2s and 2p and Si $3p\sigma$ levels. Thus the overall effect of a change in symmetry is that in a bent molecule, the two oxygen lone-pairs are described as one in a p orbital and one in an s orbital whereas in a linear molecule, the oxygen s orbital must become involved in the skeleton bonding, the lone-pairs becoming doubly-degenerate in oxygen p orbitals.

Assignment of the broad band between 12 and 13 eV is made to the Si - H and Ge - H σ levels respectively as for the halides and sulphides, the decrease from silicon to germanium being of the same order. In dimethylether the bands at 16.5 eV and 13.4 eV are assigned to mixtures of the b_2 M - O and M - H bonding levels, the a_1, a_2 and b_1 components of the M - H bonding levels occuring at 14.2 eV. Accordingly the band at 11.91 eV is assigned to the $4a_1$ C - O σ bonding level. The first band of dimethyl and digermyl ether is assigned to the Op_z $2b_1$ lone-pair level being relatively intense. On changing to D_{3h} symmetry, the doubly-degenerate e level is effectively a mixture of the $2b_1$ lone-pair and $4a_1$ Si - O σ levels, this being assigned to the broad band at 11.17 eV. The a_2'' Si - O σ bond, equivalent to the $3b_2$ level is then assigned to the band at 14.5 eV. The band at 17.2 eV is assigned to the

Si 3s electrons. This assignment fits in well with the assignment for dimethyl ether and digermoxane as well as taking into account the change in symmetry. The spectrum can, however, be assigned in terms of C_{2v} symmetry, analogous to that of the sulphide and selenide, the splitting of the lowest energy level peak being attributable to the a_1 and b_2 Si - O σ levels, but correlation to Me_2O and $(GeH_3)_2O$ becomes difficult. Since all the bands in disiloxane are broad there must be much mixing and delocalision of electrons. Thus the bonding could well be described in terms of a mixture of both analyses.

Again as for the halides and other group VI compounds, the change in I.P. of the formally oxygen lone-pair levels and their change in shape both imply $(p \rightarrow d)\pi$ bonding. The U.V. spectra of $(SiH_3)_2O$ and $(CH_3)_2O$ indicate a shift of about 1.5 eV to lower energy for the first transition. In view of the stabilisation of the first I.P. in $(SiH_3)_2O$ by only 1.1 eV, there is a possibility of the more favourable interaction between d orbitals and anti-bonding orbitals such as σ^* a_2''.

Conclusions

On the basis of the assignment made using the molecular orbital scheme, the lone-pair electrons in the compounds $(MH_3)_2Y$, (Y = S, Se, Te; M = Si, Ge), and MH_3SH are in p and s orbitals, the latter probably occuring at higher I.P. This is in accord with structural data where a skeletal angle of near 90° implies small s character and large p character in the σ bonds between Y and the MH_3 groups. The shifts in energy levels, on substituting Si or Ge for C, is evidence for $(p \rightarrow d)\pi$ bonding. In disiloxane the P.E. bands assigned to the lone-pair levels show greater bonding character, the simplest analysis implying that they

are in orbitals with little s character and greater p character compared to the other silyl derivatives allowing better overlap for $(p \rightarrow d)\ \pi$ bonding. This again is in accord with structural data.

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CHAPTER THREE

The Photo-electron Spectra of some Silyl and Germyl derivatives of the group V elements

Introduction

The silyl and germyl derivatives of the group V elements have the general formula $(MH_3)_3Z$, (M = Si, Ge, Z = N, P, As), being analogues of trimethylamine, trimethylphosphine and trimethylarsine. They are of interest as all, expecially trisilylamine, have quite a different chemistry from the methyl analogues. They do not form quaternary ammonium, phosphonium and arsonium salts and generally they show weak nucleophilic character, showing no reaction with BF_3, SiH_3I or CH_3I. They are weaker bases than methyl analogues, the reduction of base strength being proportional to the number of Si - Z bonds present as shown by the order of base strengths found for the following;

$$(SiH_3)_3N < (SiH_3)_2NCH_3 < SiH_3N(CH_3)_2 < (CH_3)_3N$$

by reaction with BF_3 [13] and the order found in the following by reaction with borane;

$$SiH_4 \ll SiH_3N(CH_3)_2 < SiH_2(N(CH_3)_2)_2 \sim SiH(N(CH_3)_2)_3 > Si(N(CH_3)_2)_4$$

steric factors becoming predominant towards the end of the series [14]. It has also been suggested that trisilylphosphine is a weaker base than monosilylphosphine from reactions with H_2S [2].

To account for this difference it has been proposed that the lone-pair on the group V atom is delocalised on to the silicon or germanium atoms by $(p \rightarrow d)\pi$ back-bonding to the empty d orbtials on Si or Ge, there being none such available in the carbon compounds. This will make the lone-pairs less available for donation to form tetra-valent Z atoms and consequently less basic, the degree of bonding increasing with number of bonds to Z.

However, trimethylamine is a weaker base than methylamine despite

an increased inductive effect making the lone-pair more available, this being due to steric effects. Similarly the large size of trisilylamine could lead to destabilisation especially in adducts where lattice energy depends on the size. It would be expected that if steric reasons were an influencing factor in decreased basicity then the increased inductive effect of the silyl group would cause the lone-pair electrons to be less tightly bound.

It has also been found that the molecular structures differ. The lack of a symmetric Si - Z stretching frequency in the I.R. spectra suggest a planar and not a pyramidal structure[1,3,4,5]. This is confirmed by electron diffraction structure determinations which indicate planar structures for the amines. Pyramidal structures with angles at Z indicating bonds to M to be intermediate between tetrahedral and perpendicular orientation are found for the phosphines and arsines, the angles in the latter being nearer 90^{o}[6,1]. Again this would be expected on postulating $(p \rightarrow d)\pi$ bonding. It has been argued that a wider angle at Z implies a greater p character in the lone-pair orbital and greater s character in the skeletal bonding orbitals leading to a planar molecule. This would similarly lead to an increased interaction between lone-pair and bonding-pair electrons. This allows a maximum overlap of p orbitals on N with the d orbitals on Si or Ge, for back-bonding to occur. In the phosphines and arsines larger p character in the σ bonds, as in the hydrides, and larger s character in the lone-pair electrons would result in the structure found but this does not necessarily rule out delocalisation of the lone-pairs by d orbital interaction. Interaction between the s type lone-pair electrons and a d orbital directed along the M - Z bonds, e.g. d_{z^2} could occur, i.e. $(s \rightarrow d)\sigma$ bonding, as has been

TABLE I

Symmetry classes of (a) valence-shell atomic orbitals and (b) molecular orbitals of $(MH_3)_3N$, (M = Si, Ge)

(a)

	a_1'	a_1''	a_2'	a_2''	e'	e''
Zn's	/					
Zn'p_z				/		
Zn'$p_{x/y}$					/	
Mns	/				/	
Mnp$_\sigma$	/				/	
Mnp$_\pi$/H1s	/		/	/	//	/
Mnd	combinations in all classes of symmetry					

(b)

	a_1'	a_2'	a_2''	e'	e''
Znp$_z$ lone-pair			$2a_2''$		
M – Z σ bonding	$2a_1'$			$3e'$	
M – H σ bonding		$1a_2'$	$1a_2''$	$2e'$	$1e''$
Mns (M – H bonding)	$1a_1'$			$1e'$	

postulated for trisilylphosphine[7]. Similarly changes in geometry from methyl compounds of silicon or germanium attached to a nitrogen have been found in silyl and germyl pseudohalides and interpreted in terms of $(p \rightarrow d)\pi$ bonding[15]. The photoelectron spectra of these compounds have been similarly interpreted as well as showing much interaction between occupied orbital levels[8].

Spectra and Assignments

The spectra are found in Figs. (I and II) and the vertical ionisation potentials in table III, together with those for the corresponding carbon compounds. The silyl and germyl amines, being planar, belong to the C_{3v} point group. The constituent valence shell atomic orbitals and molecular orbitals are shown in tables I and II. The three fold axis in both structures is considered to lie along the z axis, this being through X and perpendicular to the plane of the molecule in the two amines. The only difference between the point groups is the introduction of a horizontal plane of symmetry in trisilyl and trigermylamine which splits all the symmetry classes into symmetric and antisymmetric ones. The MH_3 p orbitals are divided into two sets; p_σ lying along the M - P bonds and p_π perpendicular to the M - P bonds. The latter combine with the hydrogen 1s orbitals to form the M - H bonding orbitals in a_1, a_2 and 2xe combinations. The Mns orbitals will also be involved in M - H bonding, in a_1 and e combinations although they will probably retain atomic character as in the halides and group VI compounds. The 3a, and 4e, or $2a_1'$ and 3e' M - Z bonding orbitals are formed by combination of the Mp orbitals with the ns and np orbitals of Z. In the pyramidal molecules bonding can occur with the Zns, Znp_x, p_y and p_z orbitals whereas in the

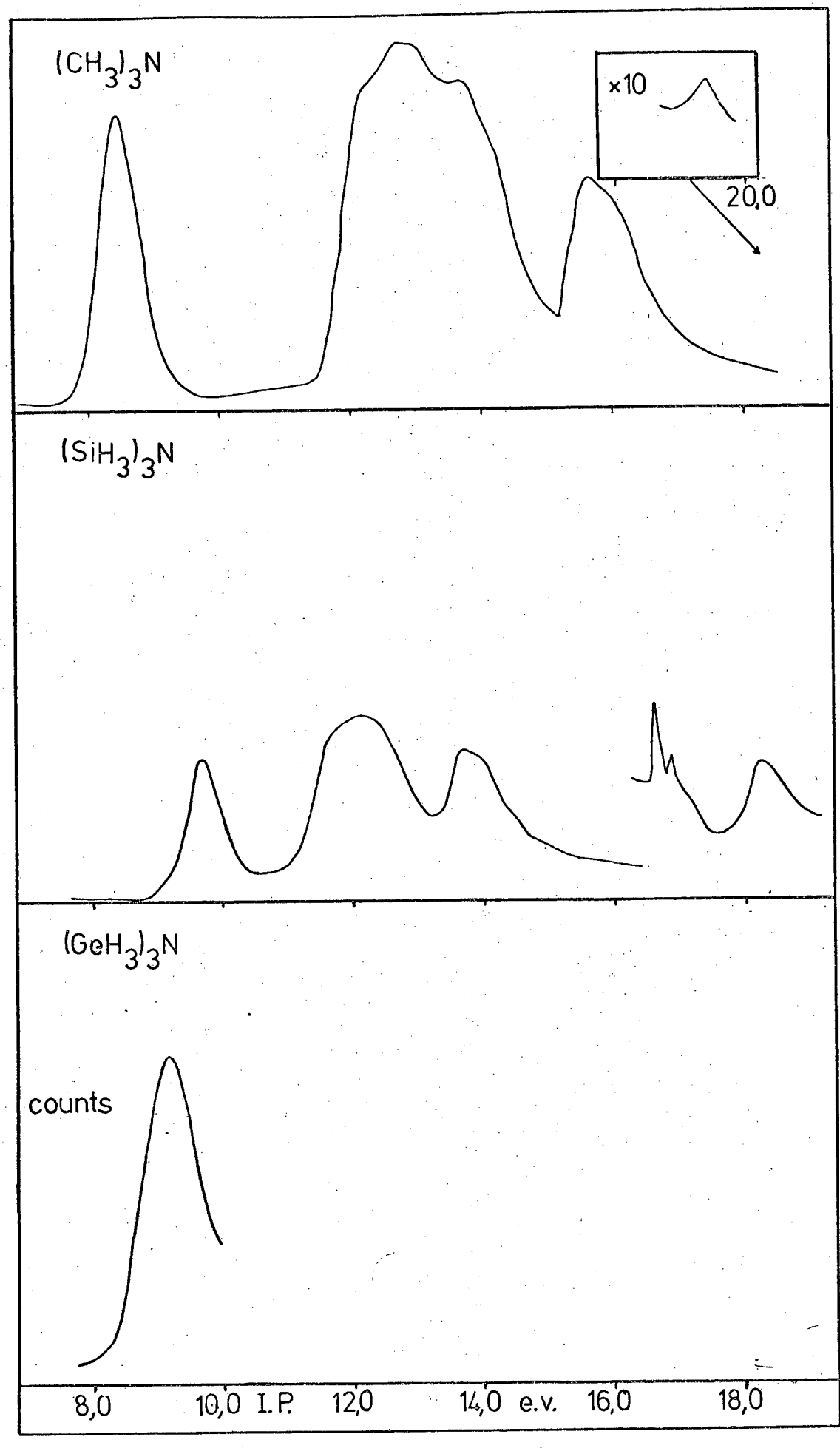

Fig I

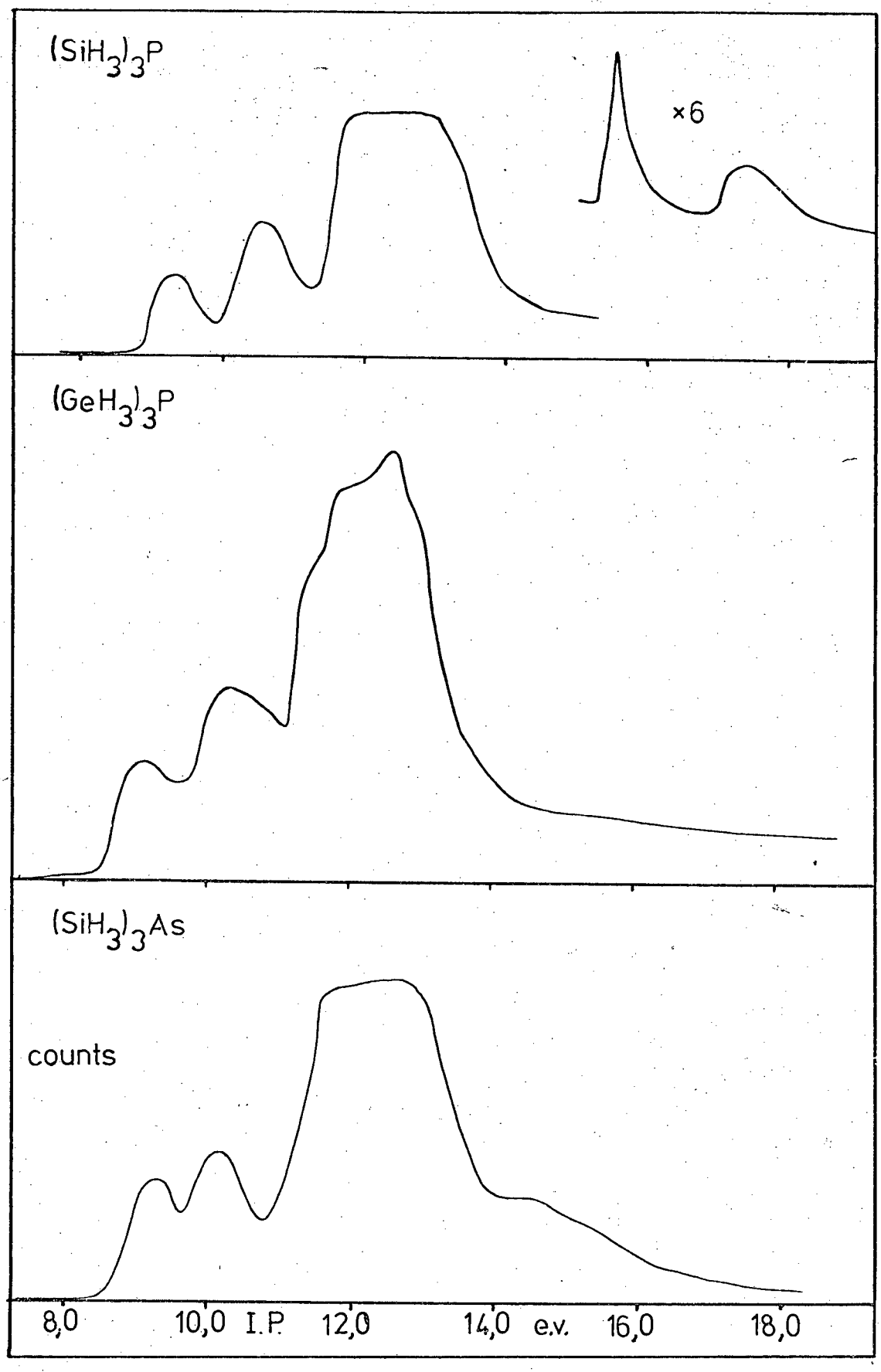

Fig II

TABLE II

Symmetry classes of (a) valence shell atomic orbitals and (b) molecular orbitals of $(MH_3)_3Z$, (M = Si, Ge, C, Z = P, As; M = C, Z = N)

(a)

	a_1	a_2	e
Zn's	/		
Zn'p_z	/		
Zn'p_x/p_y			/
Mns	/		/
Mnp_σ	/		/
Mnp_π /Hls	combinations in all classes		
Mnd	combinations in all classes		

(b)

	a_1	a_2	e
Zp_z lone-pair	$4a_1$		
M – Z σ bonding	$3a_1$		4e
M – H σ bonding	$2a_1$	$1a_2$	3e 2e
Mns	$1a_1$		1e

planar trisilyl and trigermylamines the Znp_z orbital can no longer combine with any σ orbitals on M although interaction with Mp_π is possible. On consideration of overlap, interaction between Zns and Mnp_σ is probably small, implying that $3a_1$ and $2a_1'$ may well have much Zns atomic character. Thus the $2a_2''$ level is the lone-pair level in trisilylamine and trigermylamine, corresponding to the $4a_1$ level, again Zp_z, in the pyramidal molecules. Thus the main effect of the change in symmetry is to lower the amount of possible filled orbital - orbital interaction of the Zp_z orbital. There will also be corresponding anti-bonding orbitals in all classes.

The spectra are very simple although the molecules are comparatively large, showing only five bands. This is a general feature of the P.E. spectra of large molecules and is due to the overlapping of bands. Thus a complete analysis is not possible. The spectra are also quite similar despite the different geometries of the molecules. The spectrum of trigermylamine shows only the first band as the remainder were obscured by strong bands due to germyl chloride which was present in the sample to prevent its rapid decomposition. The first band in each case is assigned to the $2a_2''$ or $4a_1$ lone-pair level by correlation with the $2a_1$ lone-pair level in the corresponding hydrides, ZH_3[10] a reduction in I.P. occurring in each case. However, unlike the hydrides no vibrational fine structure is found although the band is broad. The broad bands between 11 and 13 eV in the silyl and germyl compounds and between 12 and 15 eV in the methyl compounds are assigned to the e combinations of the M - H σ levels by comparison with the halides and group VI compounds. The assignment of the remaining strong band is made to the M - Z level, the shift from 13.7 eV in trisilylamine to 10.2 eV in trisilylarsine

TABLE III

Vertical ionisation potentials for $(MH_3)_3Z$; (M = C, Si, Ge; Z = N, P, As). (± 0.1 eV)

M	Y	$4a_1/2a_2''$	3e/2e'	MH	Mns(a_1')	Mns(e')
C	N	8.5	15.7	11.6 - 15	19.4	-
Si	N	9.7	13.7	10.8 - 13	16.6	18.2
Ge	N	9.2	-	-	-	-
C	P	8.6	11.3	12.7 - 15.8	-	-
Si	P	9.3	10.6	11.5 - 13.7	15.6	17.4
Ge	P	9.0	10.4	11.2 - 13.2	-	-
Si	As	9.3	10.2	11.5 - 13.2	14.5	-

being consistent with the changes in electro-negativity difference between Si and Z. Finally the weak bands at high I.P. are assigned to the a_1 and e combinations of the Si 3s levels, the a_1 again shifting to lower energy as the electro-negativity of Z decreases. In both trisilylphosphine and trisilylamine the a_1 level occurs at lower I.P. and is much sharper, the e level being assinged to the broader peak at higher I.P.

In all the compounds, including trimethylamine, the contour of the first band implies that the lone-pair electrons are not strictly non-bonding. Also the shift in I.P. of this level as M changes is again found to be Si > Ge > C, the opposite to that expected in terms of electro-negativity changes of M, C > Si ≃ Ge. Since for the planar molecule the lone-pair exists in the a_2'' orbital, the only unoccupied orbital available for interaction is the Mnd i.e. $(p \rightarrow d)\pi$ bonding must occur. Alternatively back-donation could occur to the empty M - H σ a_2 orbitals in the MH_3 group but such an effect would be expected to be greater for the carbon compounds than the silyl due to the poor overlap possible with the longer Si - N bonds. As there is a progressive increase in I.P. of the first band in the series $(CH_3)_3N$, $(CH_3)_2N\,SiH_3$, $CH_3N\,(SiH_3)_2$, $(SiH_3)_3N$,[11] following their base strengths, indicating a gradual electron withdrawal from the nitrogen by the silyl groups, the delocalisation is a function of the silicon atom: as carbon has no d orbitals, $(p \rightarrow d)\pi$ bonding would seem to occur. Another possibility is that the inductive effect of the MH_3 group and the polarisation of the M - N bond would cause a σ charge transfer from M to N via p σ orbitals. This is accompanied by a synergic π back-bonding of the lone-pair to the Silicon

p orbitals of the correct symmetry i.e. $(\tilde{p} \rightarrow \tilde{p})\pi$ bonding. This again would be a maximum in the planar configuration. However, in view of the constancy of the positions of the Si - H σ level, this is not considered to be the case.

It is interesting to note the change in intensity of the band due to the lone-pair electrons relative to the others as the symmetry of the molecule changes. The very low cross-section in the pyramidal arsines and phosphines implies that the orbital has s character[12] whereas the higher cross section in the planar trisilylamine implies more p character. Also the stabilisation of the lone-pair electrons in the sily compounds with respect to the methyl compounds is twice as large in the amines as in the phosphines. This is consistent with the idea that in the planar molecules, the lone-pair orbital takes on more p character increasing its back-bonding ability. Back-bonding in the pyramidal molecules can also occur by the less effective $(s \rightarrow d)\sigma$ bonding. The silicon 3s level energy decreases greatly on changing Z from N to As as is found for the monosilyl compounds (see chapter V). The first I.P.s of trimethylamine and trisilylamine are also consistent with the relative basicities of the two amines, the lone-pair being held tighter in the silyl compound and so less able to donate to form a bond. Thus relative basicities may be due to π bonding and not to steric or other effects.

Conclusions

The analysis of the relatively simple spectra of complex molecules cannot be taken as strong evidence for any postulates regarding bonding because of the large number of symmetry allowed interactions. However,

the assignments and trends of I.P.s are consistent with $(p \rightarrow d)\pi$ bonding occurring in the compounds. This occurs to a greater extent in the amines, where a planar geometry allows maximum interaction of the p type lone-pair orbital, σ bonding being via sp^2 hybrid type planar orbitals. In the pyramidal phosphines and arsines the lone-pair has more s character, delocalisation by $(s \rightarrow d)\sigma$ bonding being a possibility, the skeletal σ bonds having greater p character as predicted from geometry.

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CHAPTER IV

The Photo-electron Spectra of some Organic π bonded derivatives of the group IV elements

In this chapter, the spectra of allyl and vinyl silane and trifluorosilane, allyl and vinyl germane, silacyclopent-3-ene and its 1:1 dichloro and 1:1 difluoro derivatives are compared to their carbon analogues.

These systems are of interest as there is again a possibility of $(\pi \rightarrow d)\pi$ bonding by delocalision of the π bonds to the empty Si 3d and Ge 4d orbitals, not available in carbon, and also of $(\pi^* \rightarrow d)\pi$ bonding in excited state molecules, a bonding situation which is more favourable than $(\pi \rightarrow d)$ bonding because of the better energy matching, and so greater interaction of the two orbitals.

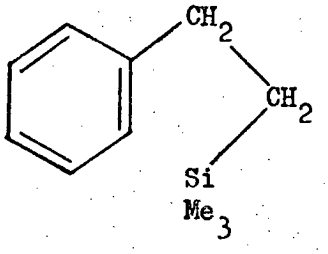
The chemistry of silyl and germyl substituted systems differs markedly from that of their carbon analogues, particularly allyl and vinyl systems[10,2]. On addition of alkyl halides to vinyl silanes, anti-Markownikoff products are found[1] whilst addition to allyl silanes gives the expected Markownikoff products[2]. Since silyl groups have a larger inductive effect than methyl groups, tending to stabilise the ionic intermediate in favour of Markownikoff addition, an opposing effect, e.g. $(\pi \rightarrow d)\pi$ bonding produces the reverse polarity needed. The abnormally high rate of polymerisation of $Me_3SiCH = CH_2$ when compared to $Me_3CCH = CH_2$ has been attributed to $(\pi \rightarrow d)\pi$ bonding[7] whilst the ease of lithium catalysed isomerisation of $Me_3SiCH = CHMe$ compared to its carbon analogue is thought to be due to $(\pi^* \rightarrow d)\pi$ bonding, promotion and delocalisation of the electrons to the silicon atom allowing rotation of the C - C bond and hence isomerisation. π bonding is also indicated by the slower rate of addition of dichlorocarbene to vinyltrimethylsilane when compared to its carbon analogue, the fast rate of addition to allyl trimethylsilane

is interpreted as being a result of the silicon inductive effect, any delocalision of the π bond being prevented by the CH_2 group intermediary between the Si 3d orbitals and the bond. This inductive effect of the Me_3SiCH_2 group is shown in the high reactivity of ally silanes to hydrogen halides HNCS and $(SCN)_2$ which is also in accord with postulated hyperconjugation i.e. inter-action between the Si - C σ bond and the C - C π bond or other bonds β to the π bond increasing the polar nature of the double bond[4]. The Markownikoff addition of hydrogen bromide to allyltrimethylsilane, even in the presence of peroxides, indicates that the process is via a polar intermediate, stabilised inductively, and not by a radical mechanism[5]. The relative strength of the inductive effect of the Me_3SiCH_2 group is demonstrated by the anti-Markownikoff addition of hydrogen bromide to $Me_3SiCH_2CH = CMe_2$[6]. The faster addition of the trichloromethyl radical to allyltrimethylsilane[9], has been postulated as occurring via an intermediate stabilised by 'though-space' $(\pi \rightarrow d)\pi$ bonding. A similar situation occurs in the slow polymerisation of allyl silanes compared to vinyl and 3 butenylsilanes, the intermediary free-radical being very stable and unreactive because of the $(\pi \rightarrow d)\pi$ delocalision [10]. The cleavage of the M - C bond, (M = Si, Sn), in allyl derivatives by electrophilic reagents e.g. mercuric halides and hydrogen halides, has been described by a mechanism involving a competition between donor-acceptor interactions between the π bond and the M atom and between the π bond and the electro-phile, $(\pi \rightarrow d)$ interaction in the tin case being strong enough to prevent cleavage[15].

There is much spectroscopic evidence for π bonding in these compounds. An investigation by Bock[11] of a series of ethylenes substituted with

trimethylsilyl groups and trimethylsilylmethyl groups is one of a series of papers on the subject. Using ground state spectroscopic techniques of I.R. and nuclear magnetic resonance, shifts in the silyl compounds are opposite to that expected in terms of simple electronegativity. Use of excited state spectroscopic techniques of U.V., electron-spin resonance spin densitites of radical anions and polarographic half-wave reduction potentials has given evidence for the more favourable ($\pi^* \rightarrow d$) π interactions. All the results with compounds containing the Me_3SiCH_2 group indicate no π bonding but a large silicon inductive effect, enhanced by the methyl groups.

Most studies so far have involved π systems substituted with $SiMe_3$ groups. A study of the bonding to silicon in these systems is complicated further by the large inductive effect of the methyl groups. Little is known of allyl silane in which there is a possibility of 'through-space' ($\pi \rightarrow d$) interactions. This has been proposed in the bonding of;



between the benzene π system and the silicon 3d orbitals[12] which stabilises the molecule holding it in one conformation. A similar interaction has also been proposed between the Si 3d orbitals and halogen lone-pair orbitals in silylmethylhalides[21]. Allylsilane may also be subject to fluxional behaviour i.e. a 'hopping' of the silyl group from one end to the other of the allyl system in which the π system becomes delocalised,

TABLE I

Symmetry Classes of (a) the valence-shell atomic orbitals and (b) molecular orbitals of $MH_3CH = CH_2$, (M = C, Si, Ge)

(a)

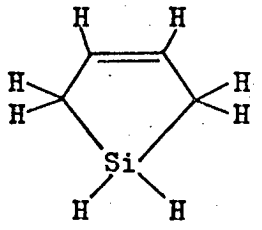
	a'	a"
H 1s	///	
C 2s	//	
C 2p	////	//
Mns	/	
Mnp_π	/	/
Mnp_σ	/	
H 1s	//	/

(b)

C – C π		2a"
C – M σ	7a'	
C – C σ	6a'	
M – H σ	5a'	1a"
C – H σ	4a'	
Mns	3a'	
C – H σ (C2s)	2a'	
C – H σ (C2s)	1a'	

as in silylcyclopentadiene[16] but no such evidence could be found, (see Appendix II).

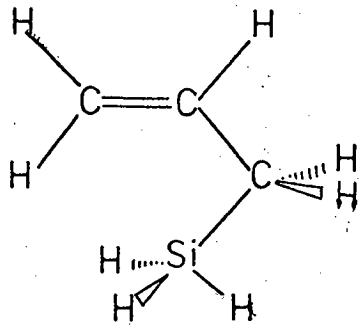
Silacyclopent-3-ene, in which the ring is planar has a similar configuration to allyl silane in that the silicon atom is β to the double bond but is now rigidly fixed, there being no rotation about the C - C bond. The molecule does have a low frequency ring being vibration[13]. There is a possibility of a transannular ($\pi \rightarrow$ d) π



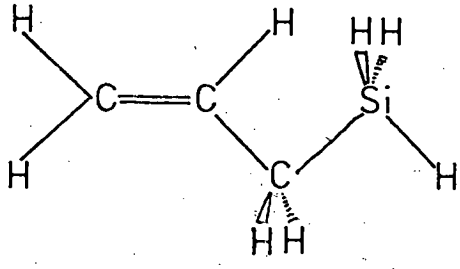
interaction which will increase the I.P. of the π bond by electron withdrawal and lead to a planar distortion of the ring as was originally proposed from I.R. studies[13], present opinion being that the ring is only slightly distorted[14]. The fixed configuration of the Si - C - C = C skeleton prevents any σ/π hyperconjugation. For this interaction the two bonds must be of the same symmetry, i.e. parallel in the molecule with respect to their constituent atomic orbials. Here the two bonds are perpendicular, the π bond being formed from C $2p_z$ orbitals and the Si - C bonds from C $2p_{x/y}$ and hence interaction is symmetry forbidden.

Spectra and Assignments

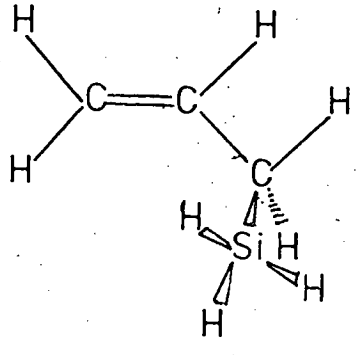
The symmetry classes of the atomic and molecular orbitals of the vinyl compounds are shown in table I. The molecular structures of the compounds have been determined by the elctron diffraction method[18,19] and found to belong to the C_2 point group, the Si - C - C skeleton lying in the plane of symmetry. The molecular orbitals thus occur in a' and



(a.)



(b.)



(c.)

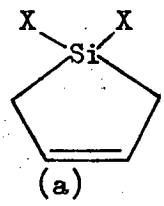
Fig I

a" combinations.

The Mnp orbitals are considered in two sets; the p_σ orbital lies along the Si - C bond and is a' and the p_π orbitals are perpendicular and parallel to the plane as so are a' and a". The p_σ orbitals combine with hydrogen 1s to give Si - H σ bonds. As for the main group silyl derivatives, the silicon 3s level is considered to retain its atomic character although it is probably involved in the bonding. The carbon-carbon and carbon-hydrogen σ bonds are found by combination of 'in-plane' C 2p orbitals with hydrogen 1s orbitals and each other. The C2s are probably involved in the bonding but considered to occur at high I.P. as for silicon, and so be undetectable by He I excitation. In vinyltrifluorosilanes, the M - H levels become M - F σ bonding and there are six extra a' and a" levels due to the combinations of Fp_π lone-pairs. Specific ordering of energy levels is then a matter for conjecture.

The ally compounds are more complex. Their symmetry is unknown so they have been assigned to the Cs symmetry class on the basis of possible equilibrium conformations due to the free rotation of the C - C bond. These are shown in Fig. I. In (a) the Si - C σ bond and C - C π bond are perpendicular. The Si - C bond is formed by combinations of 'in-plane' C2p orbitals and the C - C π bond by an 'out-of-plane' combination, the Si - C - C = C skeleton lying in the plane. Mixing of the two levels is symmetry forbidden and σ/π hyperconjugation cannot occur as in silacyclopent-3-ene. Through-space ($\pi \rightarrow$ d) π bonding will stabilise this configuration. Structure (b) has reduced H---H interactions making it energetically more favourable. (c) is a structure intermediate between (a) and (b) with no plane of symmetry. Thus the Si - C bond is parallel to the C - C π bond allowing σ/π mixing. The molecular orbital

TABLE II

Symmetry Classes of (a) valence-shell atomic orbitals and (b) molecular orbitals of;  , (M = Si, X = F, H, Cl, M = C, X = H)

(a)

	a_1	a_2	b_1	b_2
C2s	//		//	
$C2p_\pi$	////		////	
$C2p_\sigma$		//		//
Mns	/			
Mnp	/		/	/
H1s	//	/	//	/
Xns	/			/
Xnp_σ	/			/
Xnp_π	/	/	/	/
Mnd	//	/	/	/

(b)

	a_1	a_2	b_1	b_2
$C - C\pi$				$5b_2$
$C - M\sigma$	$8a_1$		$5b_1$	
Xp_π lone-pairs	$7a_1$	$2a_2$	$4b_1$	$4b_2$
$M - X\sigma$				$3b_2$
$C - C\sigma$	$5a_1$, $6a_1$		$3b_1$	
$C - H\sigma$	$4a_1$		$2b_1$	
Mns, $(M - X\sigma)$	$3a_1$			
$C - H\sigma$ (C2s)	$2a_1$	$1a_2$	$1b_1$	$2b_2$
Xns	$1a_1$			$1b_2$

scheme will be essentially similar to that of the vinyl systems. The introduction of a CH_2 group in the skeleton will lead to an extra a" level, the C – C π level becoming 3a", and of two extra a' levels, one at high I.P. and one at low I.P. Similarly there will be extra levels in the trifluoride due to combinations of the Fp$_\pi$ levels, Si – H σ bonding levels becoming Si – F σ bonding.

Thus both molecules have very low symmetry and hence much mixing of levels can occur although the a" levels have few possible interactions. There are also Mnd orbitals in both classes, 2 in a' and 3 in a".

Silacyclopent-3-ene and its derivatives are considered in terms of C_{2v} symmetry, as determined by electron diffraction. The symmetry classes of the atomic and molecular orbitals are shown in table II. The carbon 2p orbitals are divided into p$_\sigma$ orbitals in the plane of the ring and p$_\pi$ perpendicular to it. The skeletal bonding orbitals are formed by combination of the C2p$_\sigma$ orbitals and Si 3p. The Si – X σ levels are formed by combination of the Si 3p with X p$_\sigma$ in a_1 and b_2 combinations. The Xp orbitals are divided into two sets, p$_\sigma$ directed along the Si – X bond and p$_\pi$ in a plane perpendicular to the Si – X bond. Thus the only b_2 combinations are C – C π, C – H σ and M – X σ bonding. For the fluorides and chlorides there are extra levels in all classes due to the Cl p$_\pi$ or Fp$_\pi$ lone-pairs. The relative ordering will differ from that given in table II when X is fluorine, the Fp$_\pi$ lone-pairs being of higher binding energy.

The spectra are shown in Figs. II to V and the vertical ionisation potentials in tables III – V. Assignment of bands in the vinyl system is made by comparison to ethylene and to other silyl and germyl derivatives.

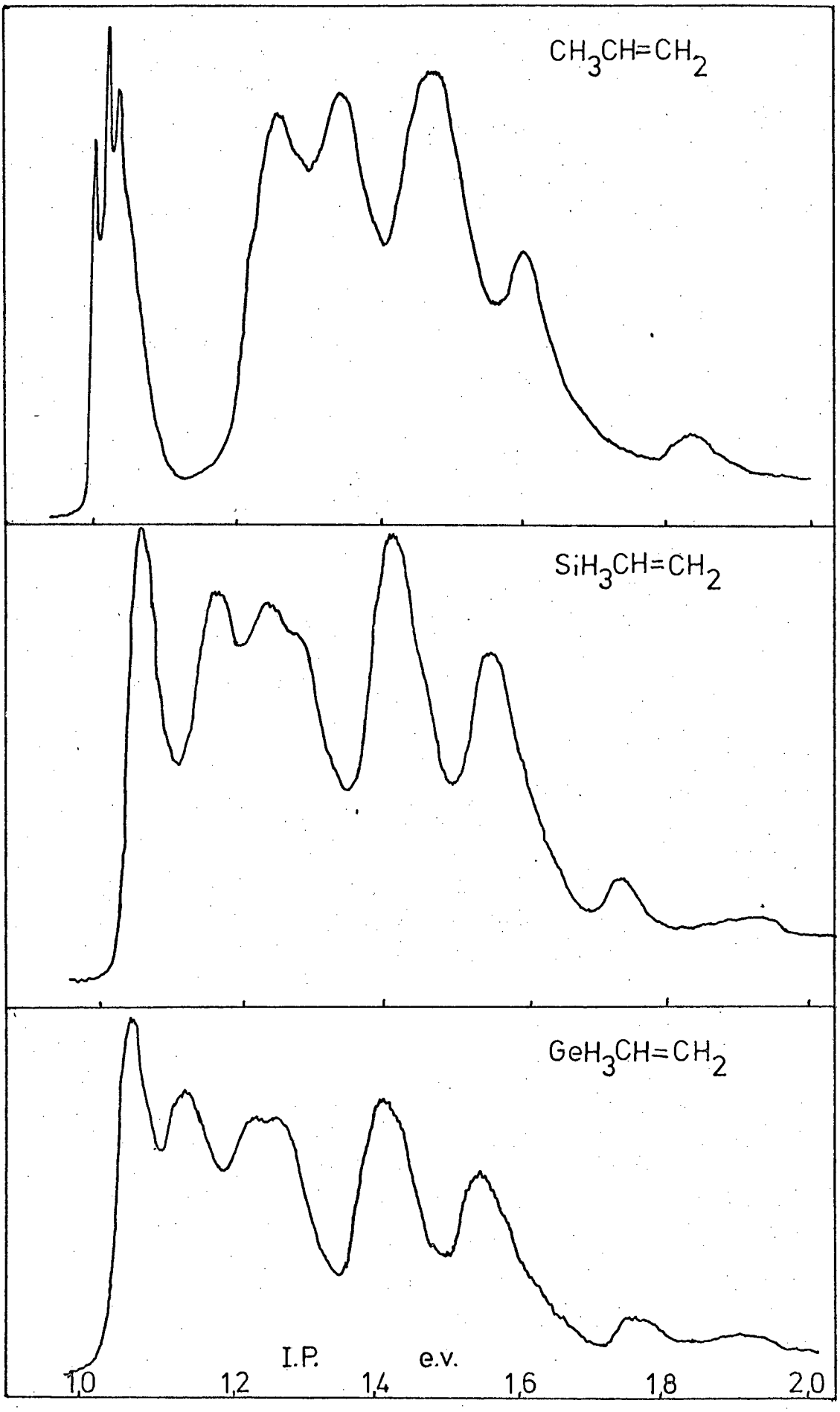


Fig II

The first band in each case is intense, showing a progression in propylene of four members with a spacing of 1340 ± 40 cm^{-1} assigned to a reduced C = C stretching frequency, (1640 cm^{-1} in the ground state). The band is thus assigned to the 2a" π level corresponding to the $1b_{1u}$ band in ethylene at 10.51 eV. The second band in the silyl and germyl compounds is assinged to the 7a' M – C σ bonding level corresponding to the 11.56 eV band in methyl silane, (see chapter V). The third band in these molecules shows a shoulder at high I.P. and is thus assigned to the 6a' and 1a" M – H levels split by interaction. In propylene the second and third bands are assigned to the 7a' C – C σ and a mixture of C – C and C – H bonding. The 6a' level corresponds to the $1b_{1g}$ level in ethylene at 12.38 eV. The next two bands in all three spectra are assigned to the C – H σ bonding and C – C σ bonding levels, the broad band in propylene at 14.53 eV probably containing the 6a' CH_3 σ electrons. The broad peak at highest I.P. in each case is assigned to the 2a' C – H σ level corresponding to the broad peak in ethylene at 18.8 eV, the $2b_{3u}$ level. The extra bands in vinyl silane and germane near 17 eV are assigned to the Mns electrons being similar to the positions of the a_1 levels in silane and germane. Considering vinyltrifluorosilane, the first two bands are assigned to the a" C – C π level and a' Si – C σ level. The C – C and C – H σ levels are now stablised resulting in a coincidence of bands above 14 eV, there being thirteen possible occupied levels; 6 Fp π lone-pair, 3 Si – F σ, 1 C – C σ and 3 C – H σ.

The spectrum of vinyltrimethylsilane shows two broad humps. The first has three maxima, assigned to the a" C – C π level, a' and a" Si – C σ levels in order of increasing I. P. The second band is assigned to a mixture of C – H and C – C σ levels.

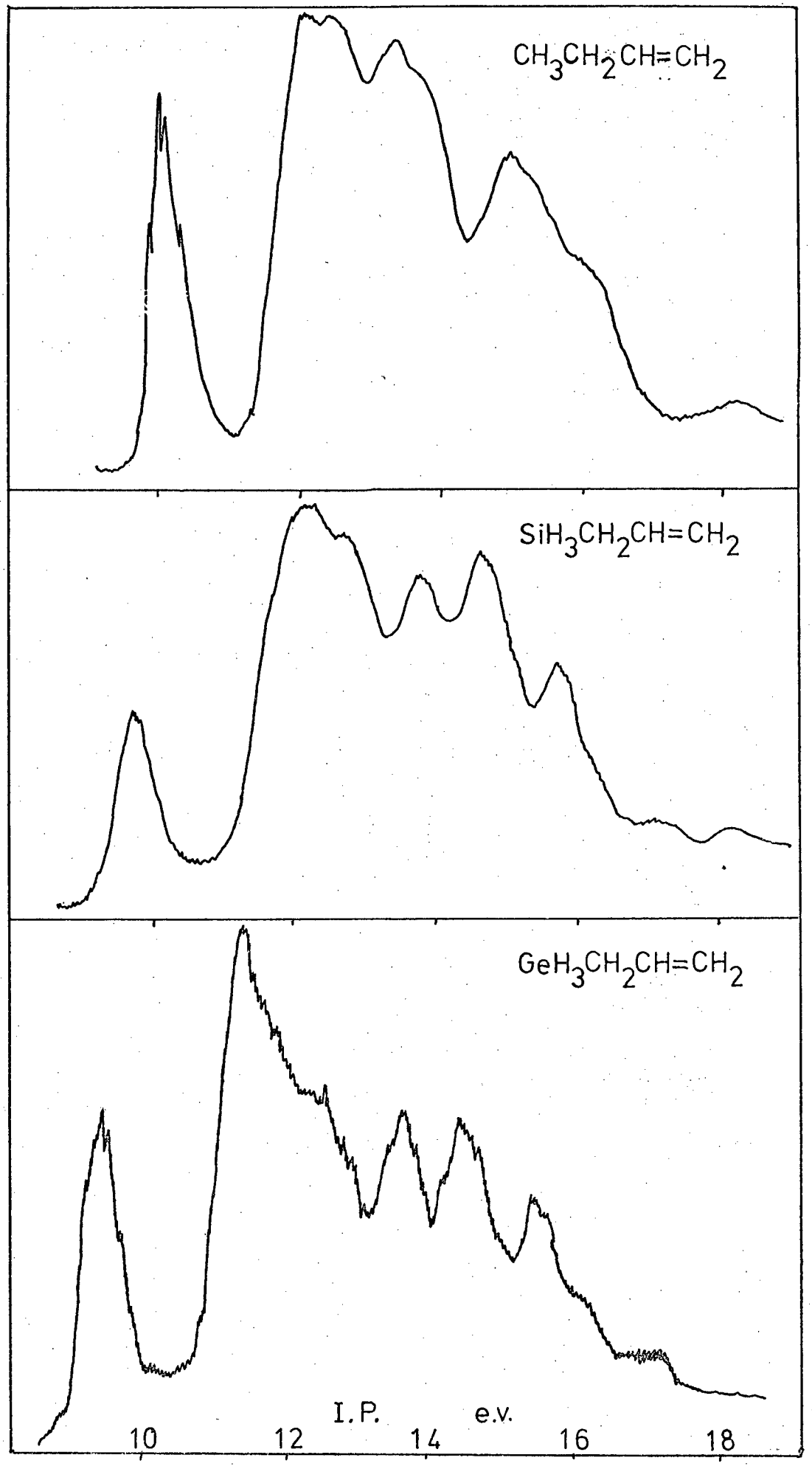


Fig III

Assignment of bands in the allyl systems is similar although it is not possible to assign all the bands because of the complexity of the molecule and the many interactions that can occur. The first band can be assigned to the 3a" π level, but-1-ene showing a progression of three members with a spacing of 1300 $\pm$ 40 cm^{-1} consistent with a reduced C - C stretching vibration, (G.S. frequency 1670 cm^{-1}). The second band is broad in all cases but the first maximum is assigned to the M - C a' σ level and the second in allyl silane and germane to the M - H σ levels. The third, fourth and fifth bands are assigned to mixtures of C - C and C - H levels. Again there is a weak band at high I.P. correlating with the $2b_{3u}$ band in ethylene. The extra bands at 17.21 and 17.19 eV in allyl silane and germane are assigned to the Mns levels. The spectrum of the fluorinated derivative is quite different. The first band at 10.43 eV is assigned to the C - C π level and the first maximum of the second band to the Si - C σ level, stabilised on comparison to the hydride. The remaining bands are assigned to mixtures of C - C, C- H, Si - F and Fp π lone-pairs, the Si - F σ bonding levels probably occurring at highest I.P.

Of the fourteen bonding electron pairs in silacyclopent-3-ene, sixteen are supplied from carbon, eight from hydrogen and four from silicon. The carbon 2s are assumed to be mainly atomic in character and occur at high I.P. Thus only ten bonding pairs are accessible to He I ionisation, as are found. The band at lowest I.P. is assigned to the $5b_2$ C- C π bond and the second and third to 8a' and $5b_1$ Si - C σ levels. The remainder are not assigned individually as they are probably well mixed. Similarly the chlorine and fluorine derivatives are

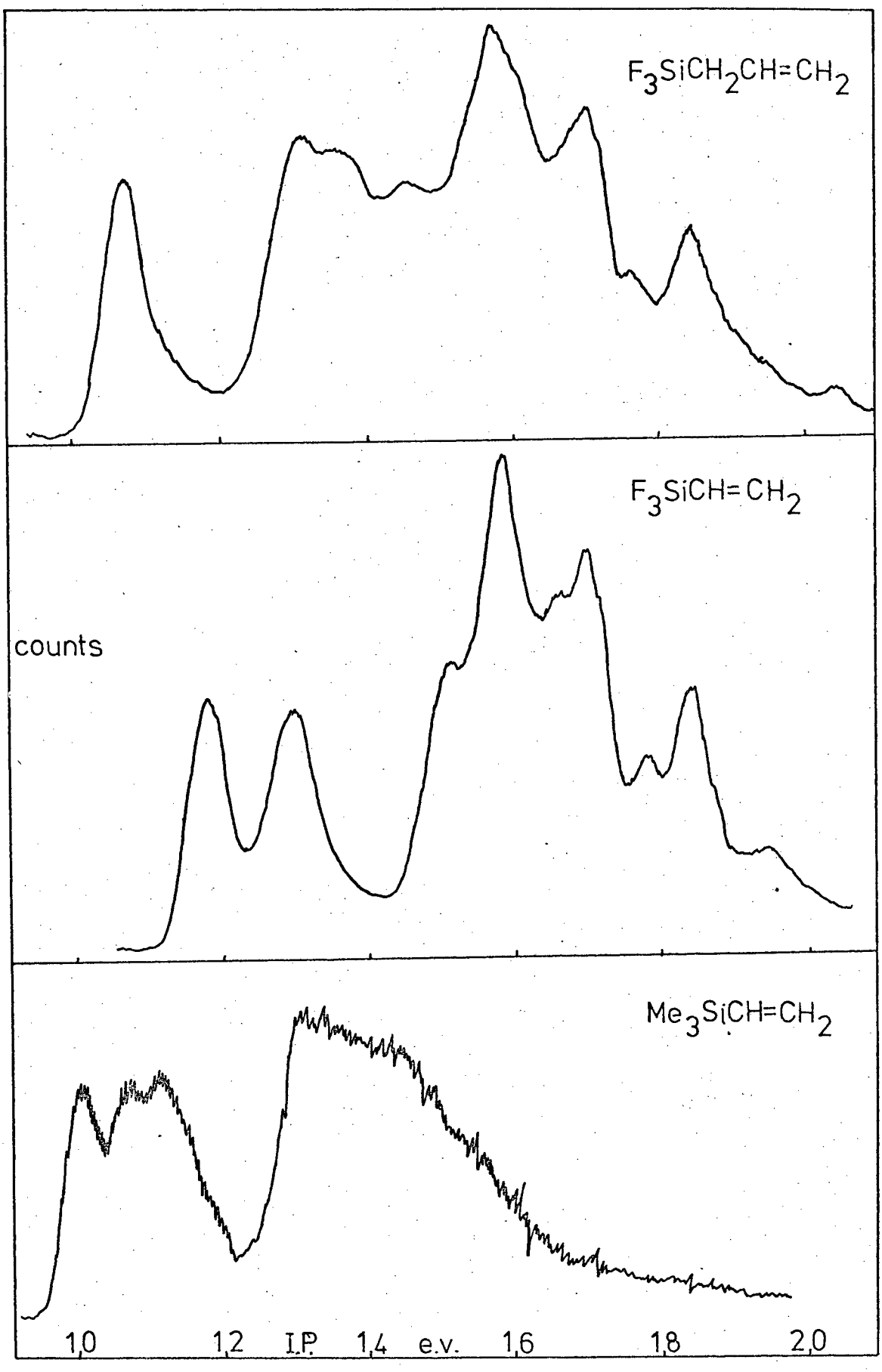

$F_3SiCH_2CH=CH_2$
$F_3SiCH=CH_2$
counts
$Me_3SiCH=CH_2$
1,0
1,2
I.P.
1,4
e.v.
1,6
1,8
2,0

Fig IV

more complex and only the first two bands can be assigned with any certainty to the C - C π and Si - C σ bonding levels.

Discussion of the bonding in the compounds is with reference to the first few bands only in each spectrum.

Considering the vinyl systems, the most striking difference in the spectra is the change in I.P. of the C - C π level as M changes from C to Ge, being of the order Si > Ge > C. This would be expected to follow the change in electrnegativity of M, but the results are in accord with ($\pi \rightarrow$ d)π bonding.

Considering vinyltrimethylsilane, the methyl groups will tend to raise the π energy level by inductive stabilisation as will the silicon atom by σ donation. However ($\pi \rightarrow$ d)π back-bonding can also occur. Since the I.P. of the π electrons is almost identical to propylene it could be argued that the opposition of these effects is equal to the inductive effect of the methyl group. However substitution of a methyl group introduces an a" Si - C level which can interact with the π level by σ/π hyperconjugation. This would seem to occur as the energies of the Si - C σ orbitals have been separated. This kind of interaction with the a" level of vinyl-silane is not thought to occur as the M - H levels are at lower I.P. than is usually found in silyl derivatives. The shoulder of the third band is assigned to the 6a' C - C σ level rather than to an Si - H σ level because of correlation with the corresponding peak in propylene at 12.39 eV.

The stabilisation of the π level in $CF_3CF = CFCF_3$[17] is only 1 eV over that in ethylene thus the similar stabilisation in vinyl-trifluorosilane is very high, possibly due to better ($\pi \rightarrow$ d)π back-bonding with the d orbitals which will be contracted by the fluorine atoms. The

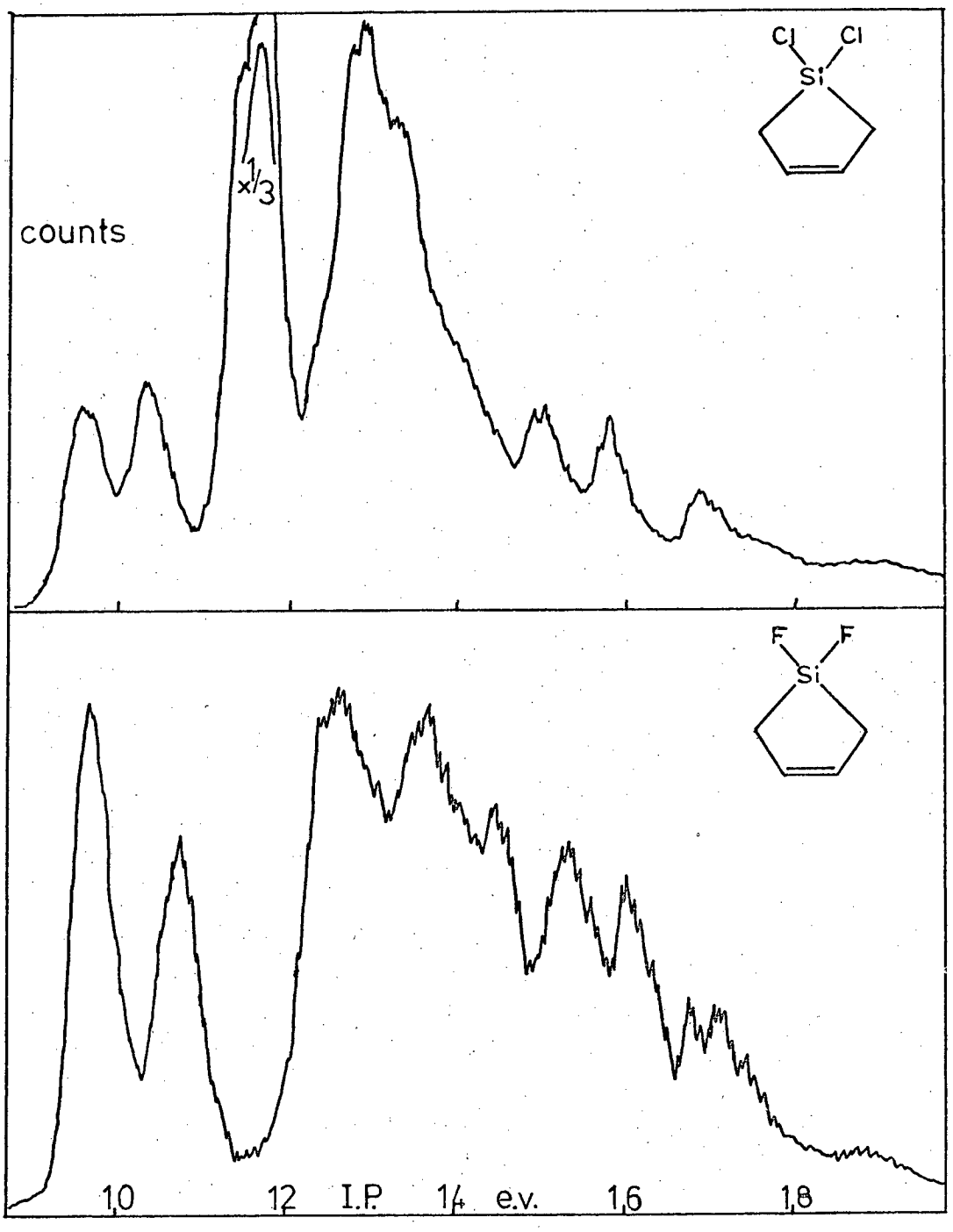


Fig V

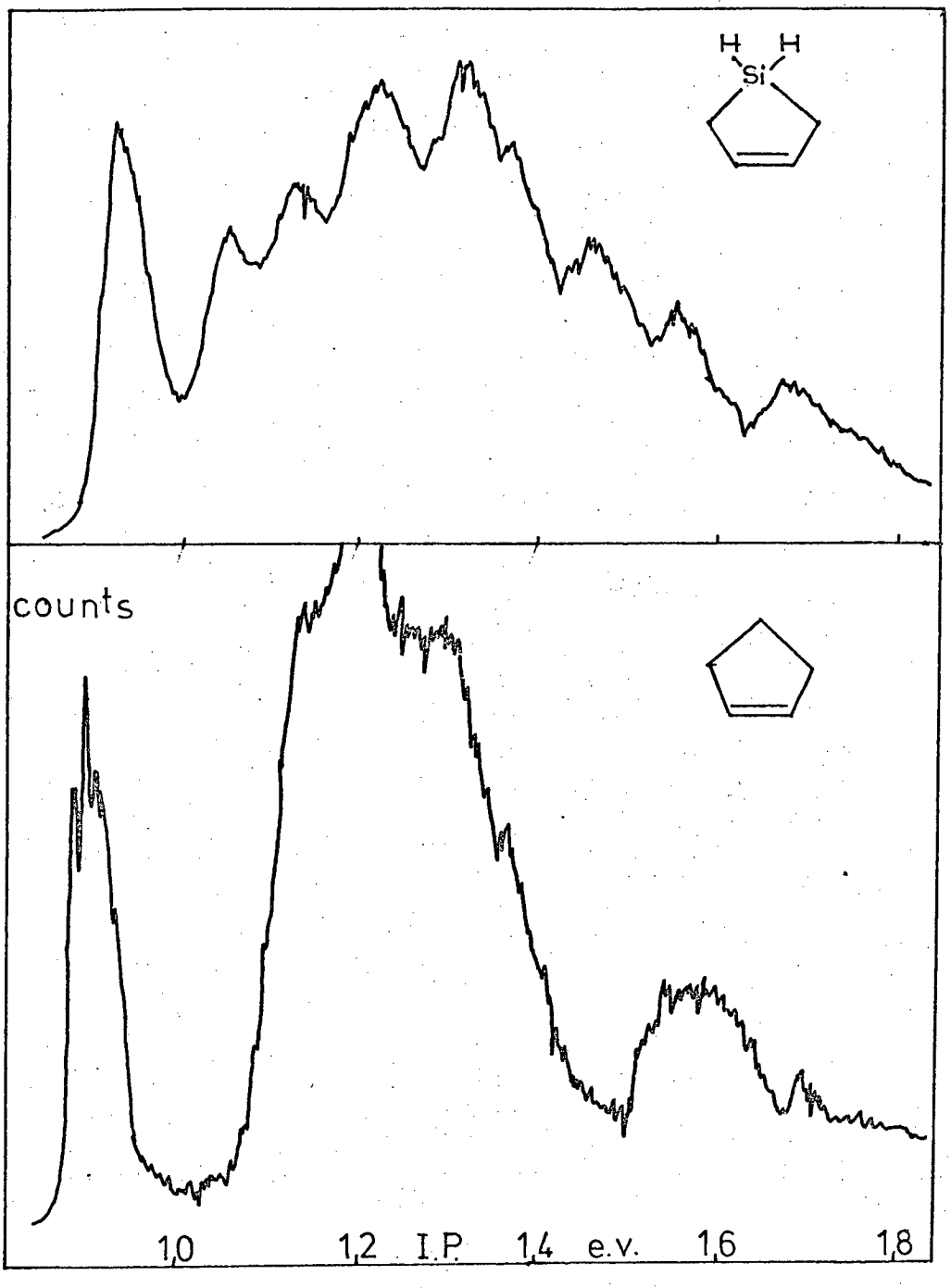


Fig VI

broad weak band at high I.P. appears to decrease in I.P. possibly due to interaction with the C - C σ level; computed energy levels for ethylene indicate C - C σ bonding in this level.

In the allyl systems, the change in I.P. is consistent with electronegativity changes of M, decreasing as M changes from Si to Ge. However, the shift in the Si - C σ bonding level from vinyl silane is large indicating a possible interaction between the two, i.e. σ/π hyperconjugation. However, since the π level in the germyl compound is destabilised 3 fold compared to the silyl, there is also the possibility of a stabilising through-space interaction. In allyltrifluorosilane, the stabilisation of the Si - C σ level is about 1 eV whereas that of the π level is only 0.5 eV again any increase in back bonding not occurring. Whilst obtaining these results, a paper appeared on the P.E. S. of allyltrimethylsilane reporting evidence for σ/π hyperconjugation and citing the possible structure as the non-planar type[24]. Thus until the structures of the molecules are known precisely, it is difficult to say if such interactions are real.

Considering the cyclic systems, the structures of the hydride and chloride have been determined and were found to be almost regular rings, there being slightly more distortion in the chloride than the hydride. The details are discussed in Appendix I. On substituting a silicon atom for a carbon atom in the ring, the I.P. of the π level is increased indicating a delocalisation of the level. This can occur by interaction with any b_2 mode but the most favourable energetically is the Si 3d. This shift in I.P. is the opposite expected from the electronegativity change. As chlorine is substituted for hydrogen, the d orbitals become contracted due to the high electro-negativity of the chlorine, better

energy matching occurs and the effect increases. This does not appear to be solely due to the electron withdrawal by the chlorine as the energy of the Si – C σ level remains quite constant. On substituting fluorine, the binding energy of the π level decreases slightly and that of the Si – C level increases indicating a possible interaction between the two. On changing the substituent at X, the centre of energy of the two bands lies on a straight line indicating a general stabilisation with electronegative substituents. Here σ/π hyperconjugation is not possible assuming a planar structure for the fluoride[14]. It is possible that the strongly electron withdrawing fluorine could cause the skeleton to become non-planar giving a puckered ring where hyperconjugative interaction could occur. In view of the first order ^{1}H.N.M.R. spectrum showing coupling between the fluorines and protons, this seems unlikely. Alternatively there could be an interaction between the low lying b_2 Si – F σ and Fp$_\pi$ b_2 levels and the C – C π level, but there is no indication of such an interaction in the chloride where the chlorine lone-pair level at 11.85 eV agrees well with those in Me_2SiCl_2 at 11.5 and 11.9 eV[25].

Whilst carrying out this work a paper appeared reporting the P.E. spectra of 1:1 dimethyl-1-sila and germapent-3-ene negating the influence of d orbitals in trans-annular bonding.

It is interesting to compare the positions of the firs two bands in allyl-silane to those of silacyclopent-3-ene, their separation decreasing from 2.35 eV to 1.25 eV respectively. Thus it would appear that σ/π hyperconjugation is significant indicating the structure of allyl silane to be non-planar.

The effect of a Silicon atom on the anti-bonding orbitals could not be determined as no ultra-violet absorbtions could be found in the range of the instrument used, (50,000 cm^{-1}).

Conclusions

From their photoelectron spectra, it appear that ($\pi \rightarrow d$) π bonding does occur in vinylsilane and germane. The bonding is allyl and cyclic systems is more complex, there being evidence for both ($\pi \rightarrow d$)π back-bonding and σ/π hyperconjugative interactions.

TABLE III

Vertical ionisation potentials of (a) $MH_3CH = CH_2$ and (b) $Y_3SiCH = CH_2$. (M = C, Si, Ge; Y = F, CH_3). ($\pm$ 0.02 eV)

(a)

M =	C	Si	Ge
2a" (C – Cπ)	10.01	10.53	10.37
7a' (C – Mσ)	12.39	11.32	11.13
1a" (M – Hσ)	13.31	12.33	12.13
6a' (M – Hσ)		12.78	12.43
5a' (C – Cσ)	14.53	14.04	13.93
4a' (C – Hσ)	15.76	15.36	15.92
3a' (Mns)		17.16	17.35
2a' (C – Hσ)	18.12	18.80	18.95

(b)

Y =	F	Me
	11.60	9.97
	12.81	10.80
	14.86	11.08
	15.57	12.16
	16.37	
	16.74	
	17.57	
	18.18	
	19.17	

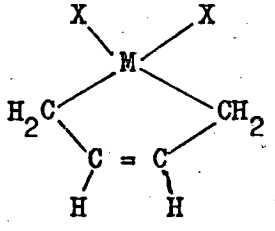
TABLE IV

Vertical ionisation potentials of $MH_3CH_2CH = CH_2$ (± 0.02 eV, (M = C, Si, Ge) and $SiF_3CH_2CH = CH_2$

	C	Si	Ge	Si F_3
3a" C = C π	9.92	9.81	9.35	10.43
9a' C – M σ	12.05	12.17	11.25	12.93
	12.36	12.83	12.47	13.43
	13.22	13.78	13.63	14.35
	14.86	14.76	14.50	15.49
	15.91	15.70	15.55	16.81
	18.01	17.21	17.19	17.46
		18.18		18.23
				20.13

TABLE V

Vertical ionisation potentials for some cyclic olefins (± 0.02 eV)



X	M	
H	C	9.00, 11–15.0, 15.5–17.0
H	Si	9.21, 10.47, 11.13, 12.46, 13.10, 13.70 14.76, 15.65, 16.83, 17.26
Cl	Si	9.63, 10.49, 11.82, 12.55, 13.48, 15.20, 15.98, 17.09
F	Si	9.62, 10.75, 12.70, 13.74, 14.51, 15.44, 16.04, 16.90, 17.20

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CHAPTER FIVE

The Photoelectron Spectra of the Iso-electronic Series;

SiH_3Cl, SiH_3SH, SiH_3PH_2, SiH_3SiH_3

and SiH_3Br, SiH_3SeH, SiH_3AsH_2, SiH_3GeH

Introduction

Iso-electronic molecules are related molecules that contain the same number of valence shell electrons although they may contain different numbers and types of atoms e.g. CO_2 and HNCO. It is found that iso-electronic molecules have very similar physical properties e.g. CO and N_2[1], although chemically they may differ greatly e.g. NaCl and NH_4Cl.

The photoelectron spectra of iso-electronic molecules are useful in the assignment of bands in a spectrum from the relative positions of energy levels. They should also reflect the changes in the nature of the substituent iso-electronic groups on the energy levels of the molecules. A number of studies of iso-electronic molecules have been made. The changing of the orbitals of neon by abstraction of protons from its nucleus, so altering the symmetry and degeneracy of the molecular orbitals, to form the hydrides, HF, H_2O, NH_3 and CH_4, shows the large variation in energy that can occur in iso-electronic molecules. The energy level splitting is progressive decreasing from about 28 eV in neon, where the lowest level is 49 eV, to 9 eV in methane where the lowest level has been raised to 23 eV[2]. The P.E. spectrum of thiazyl fluoride has been found to be very similar to iso-electronic sulphur dioxide although the apparent valence-bond structures would appear to be different according to their bond stretching constants, viz. $N \equiv S - F$ and $O = S = O$[3]. The spectra of diacetylene, cyanoacetylene and cyanogen (i.e. $X \equiv C - C \equiv X$, X = CH or N), are very similar, fine structure on certain corresponding bands being assigned to the excitation of similar vibrations[4]. The spectra of iso-electronic molecules are most easily compared in correlation diagrams based e.g. the correlation of N_2O, CO_2 and HNCO[4].

TABLE I

Vertical ionisation potentials of the iso-electronic derivatives of silane and methane. (a) 2nd row derivatives of silane, (b) 3rd row derivatives of silane, (c) 2nd row derivatives of methane.

(± .02 eV or ± .1 eV)

(a)

SiH_3SiH_3	SiH_3PH_2	SiH_3SH	SiH_3Cl
10.78	9.90	9.97	11.61
12.04	11.60	11.75	13.4
12.94	12 - 13.3	12.5	13.7
16.48	13.6	14.41	18.04
17.34	16.8		
	(re. 5)		

(b)

SiH_3GeH_3	SiH_3AsH_2	SiH_3SeH	SiH_3Br
10.17	9.77	9.45	10.96
11.67	11.09	11.24	11.10
12.67	12.08	12.67	12.85
	12.89	14.37	13.3
	16.80		18.1
	20.0		19.5

(c)

CH_3SiH_3	CH_3PH_2	CH_3SH	CH_3Cl
11.56	9.6	9.44	11.28
11.93	12.4	12.0	
13.99	13.0	13.7	14.4
16.89	14.8	15.1	15.5
	(ref. 5)	(ref. 5)	(ref. 4)

TABLE II

Symmetry classes of (a) atomic orbitals and (b) molecular orbitals of SiH_3ZH_2, (Z = P, As)

(a)

a'	a"
Si 3s	Si 3py
Si 3pz	H 1s
Si 3py	Z npx
2xH 1s	H 1s
Z ns	
X npz	
X npy	
H 1s	

(b)

Z – H anti-bonding	9a'	Si – H anti-bonding	4a"
Si – H anti-bonding	8a'	Z – H anti-bonding	3a"
Si – Z anti-bonding	7a'	Si – H bonding	2a"
Z – H anti-bonding	6a'	Z – H bonding	1a"
Z npx	5a'		
Si – Z bonding	4a'		
Si – H bonding	3a'		
Si – H (Mainly Si 3s)	2a'		
Z ns /ZH	1a'		

The P.E. spectra of the series SiH_3X, (X = Cl, Sh, PH_2, SiH_3 or X = Br, SeH, AsH_2 or GeH_3) were studied because of the possibility of $(p \rightarrow d)\pi$ bonding from the substituents as the donor properties of the substituents change. Also of interest is the effect of the changing symmetry on the molecular energy levels.

Spectra and Assignments

The vertical ionisation potentials are shown in table I and the spectra in figures I to III and correlation diagrams (I to III) along with those of the methyl second row compounds for comparison, (4) and (5). As the molecules in the series change, so their symmetry changes; SiH_3X - C_{3v}, SiH_3YH, - C_2, SiH_3ZH_2 - C_s, SiH_3SiH_3 - D_{3h} - and SiH_3GeH_3 - C_{ev}.

Molecular orbital models for SiH_3X and SiH_3YH have been set up in chapters I and II. Silyl phosphine and arsine are assumed to have C_2 symmetry, the plane of symmetry lying along the H - Si - Z skeleton, the z axis along the Si - Z bond and the x axis in the plane of symmetry to make comparison with MH_3YH easier. The symmetry classes of the atomic valence shell and molecular orbitals are shown in table II. The only orbitals in the a" class will be Si - H and Z - H σ bonding and σ^* anti-bonding orbitals formed by out-of-plane combinations of the Si $3p_x/p_y$ and Z p_y orbitals with the hydrogen 1s, the latter giving better overlap than Zp_x although they may be slightly involved. There are also a' Si - H and Z - H levels formed by in-plane combinations, the 2a' being mostly Si 3s and the 1a' mostly Zns which have I.P.s near 20 eV for both Phosphorus and Arsenic and may be undetectable. The remaining a' levels are the 5a' Zp_x lone-pair level, and 4a' Si - Z level formed by combin-

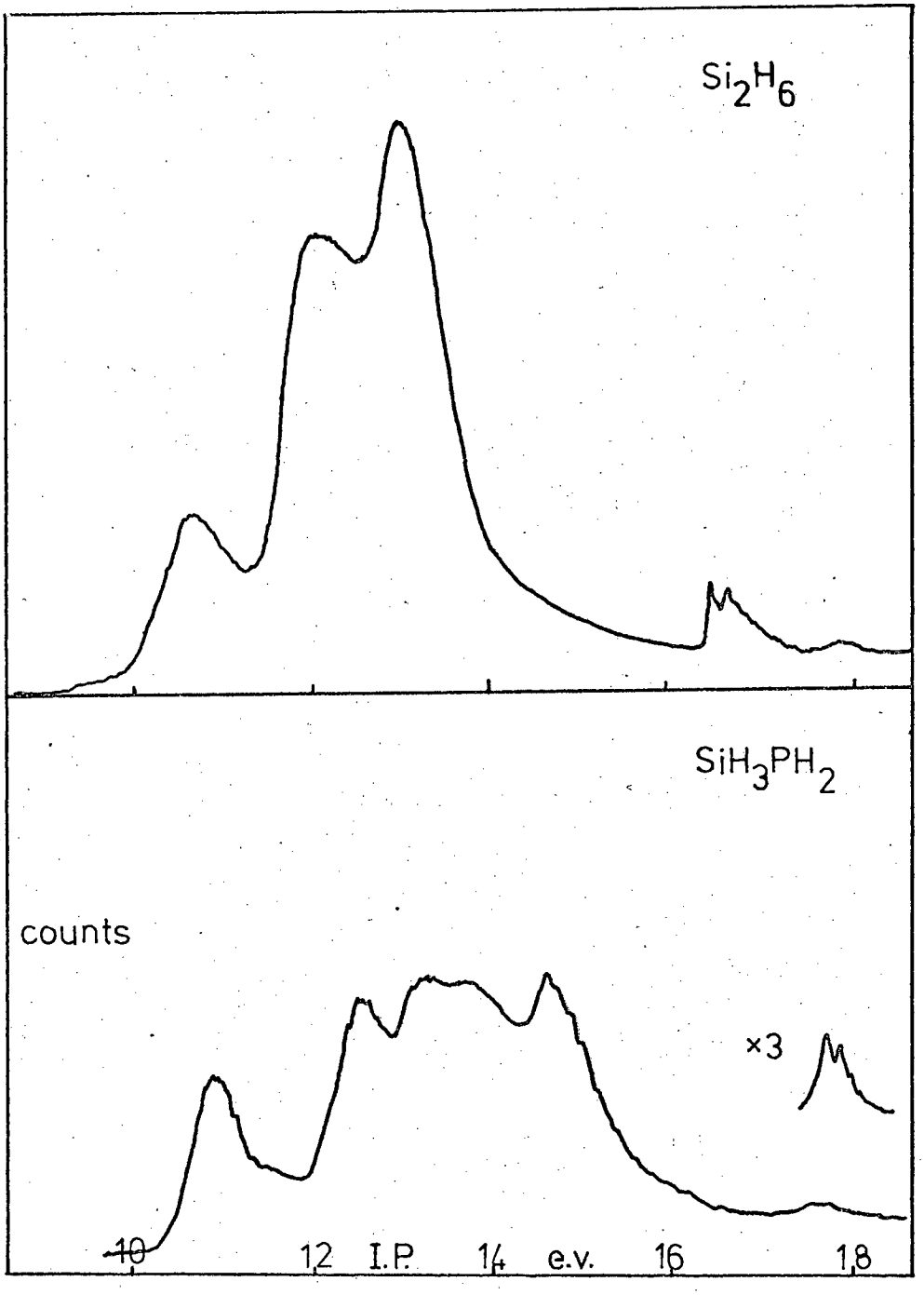


Fig I

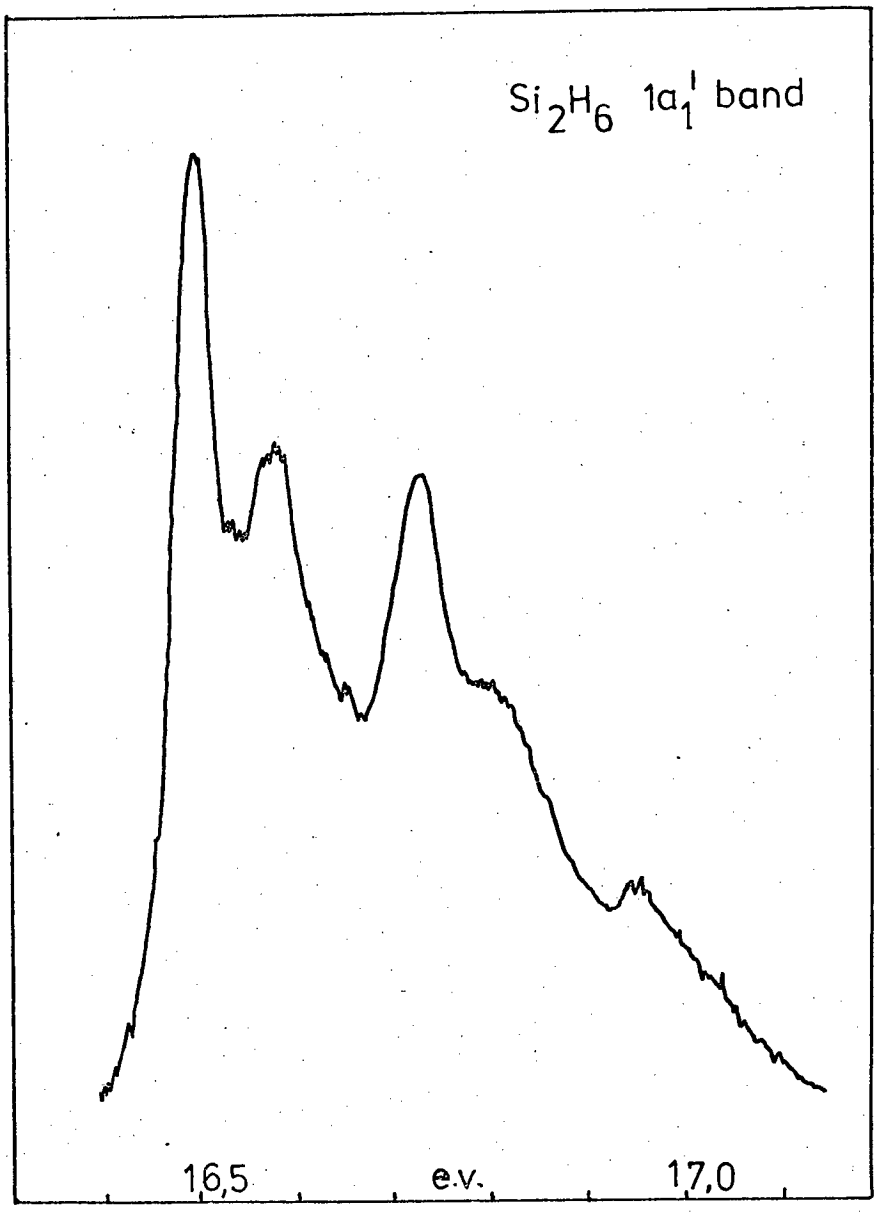


Fig La

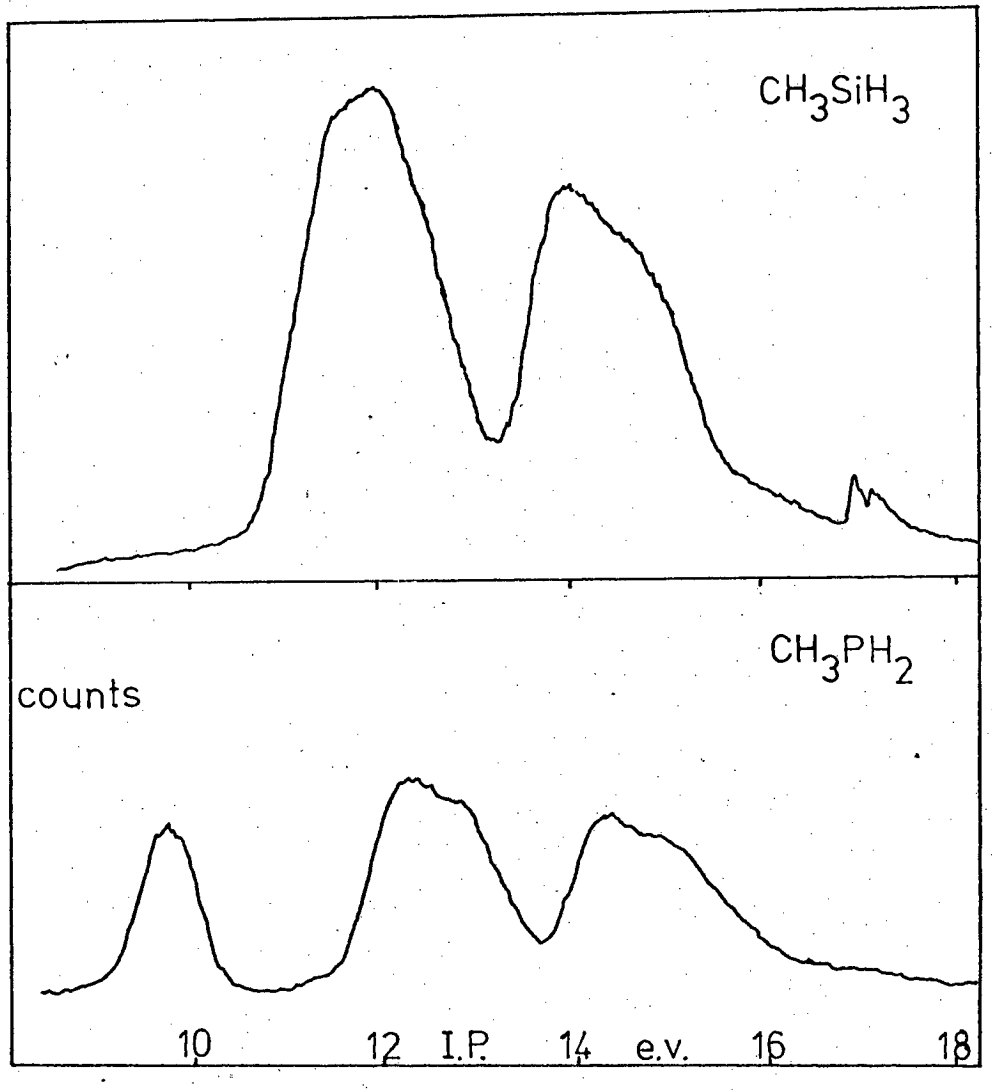


Fig II

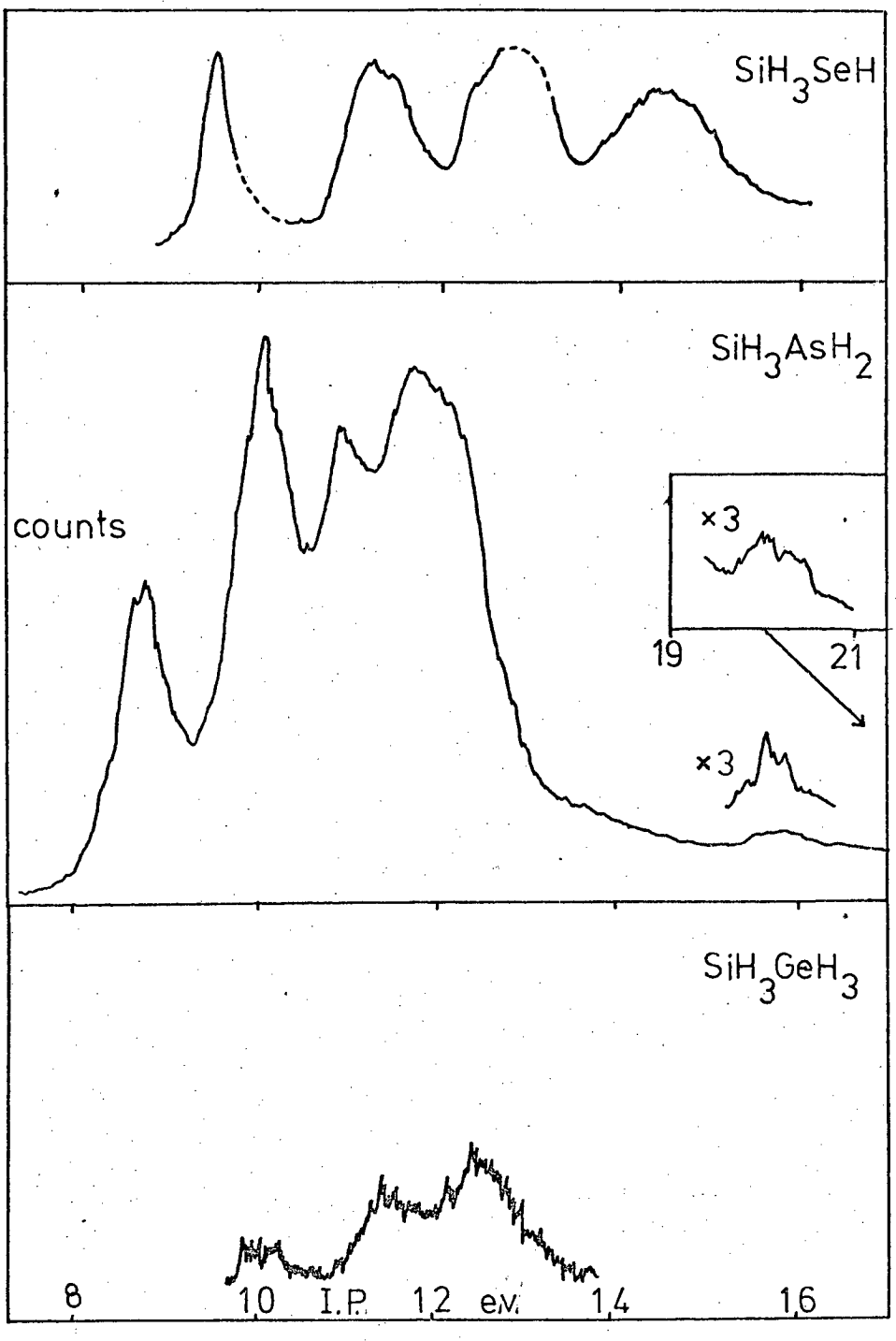


Fig III

TABLE III

Symmetry classes of (a) atomic orbitals and (b) molecular orbitals of SiH_3SiH_3. (D_{3h})

(a)

	a_1'	a_2''	e'	e''
Si 3s	/	/		
Si 3pz	/	/		
Si 3px/py			/	/
H 1s	/	/	/	/

(b)

Si - H anti-bonding	$3a_1'$	$3a_2''$	$2e'$	$2e''$
Si - Si anti-bonding		$2a_2''$		
Si - Si bonding	$2a_1'$			
Si - H bonding			$1e'$	$1e''$
Si - H bonding (mainly Si 3s)	$1a_1'$	$1a_2''$		

ation of the Si $3p_z$ and Xnp_z levels. Anti-bonding levels also occur, the 6a', 7a', 8a' and 9a' levels describing the Si - H, Si - Z, Si - H and Z - H σ bonds. The assignment of bads is shown in correlation diagrams I and II.

Five bands are found for the phosphine and six for the arsine, the fifth, near 17.0 eV in each case being assigned to the Si 3s level. The first band is assigned to the 5a' Zp_x lone-pair level and the second to the 4a' Si - Z σ bond as in the fully substituted phosphine and arsine. The third band, which is broader in the phosphine is assigned to the 3a' and 2a" Si - H levels, and the I.P. is similar to values for the halides and group VI compounds. The last band is assigned to the 1a" Z -H levels being similar in position to the 1e levels of phosphine and arsine which occur at 13.4 and 12.7 eV respectively[2]. There is probably considerable mixing between the Si - H σ and Z -H σ a' and a" levels as has been predicted from calculations on CH_3SH[7].

For disilane of D_{3h} symmetry, the constituent atomic and molecular orbitals are shown in table III. The x axis is taken along the Si - Si bond and the vertical planes of symmetry along the H - Si - Si - H skeletons. The atomic orbitals are only found in a_1', $a_2"$, e' and e" classes. The Si - Si bond is formed from a combination of the Si $3p_z$ orbitals, and a_1' combination giving a bonding orbital and an $a_2"$ an anti-bonding one. Similarly there will be a_1' and $a_2"$ combinations of the Si 3s levels which will probably be involved in Si - H σ bonding as in silane. Finally the Si $3p_x$ and $3p_y$ orbitals combine with H 1s levels to give the 1e' and 1e" Si - H bonding and the 2e' and 2e" Si - H σ* anti-bonding levels. The assignments are shown in correlation diagram I.

TABLE IV

Symmetry classes of (a) atomic orbitals and (b) molecular orbitals of SiH_3MH_3, (M = C, Ge)

(a)

a_1	e
Si 3s	Si 3px/py
Si 3pz	H 1s
H 1s	M npx/py
M ns	H 1s
M npz	
H 1s	

(b)

M - H anti-bonding	$6a_1$	Si - H anti-bonding	4e
Si - H anti-bonding	$5a_1$	M - H anti-bonding	3e
Si - M anti-bonding	$4a_1$	M - H bonding	2e
Si - M bonding	$3a_1$	Si - H bonding	1e
Si - H bonding (Si 3s)	$2a_1$		
M - H bonding (Mns)	$1a_1$		

Again the level at highest I.P. is assigned to the Si 3s $1a_1'$ levels, as for the $1a_1$ level in silane, showing two progressions of three members each of spacing 1920 cm^{-1} separated by 720 cm^{-1}. These are assigned to reduced symmetric Si - H stretching and Si H_3 deformation frequencies, ground state values from Raman spectra being 2179 and 843 cm^{-1} [8].

A broad but very weak band at 17.34 eV is also found and assigned to the $1a_2''$ Si - Si anti-bonding combination. The first, weak, band is assigned to the $2a_1'$ Si - Si σ level and the second and third, of greater intensity, to the Si - H σ levels, the $1e''$ being at lower energy corresponding to the $1e_g$ band in ethane[9]. It is interesting to note that no Jahn-Teller splitting is observed on these bands, thought it is in silane and ethane.

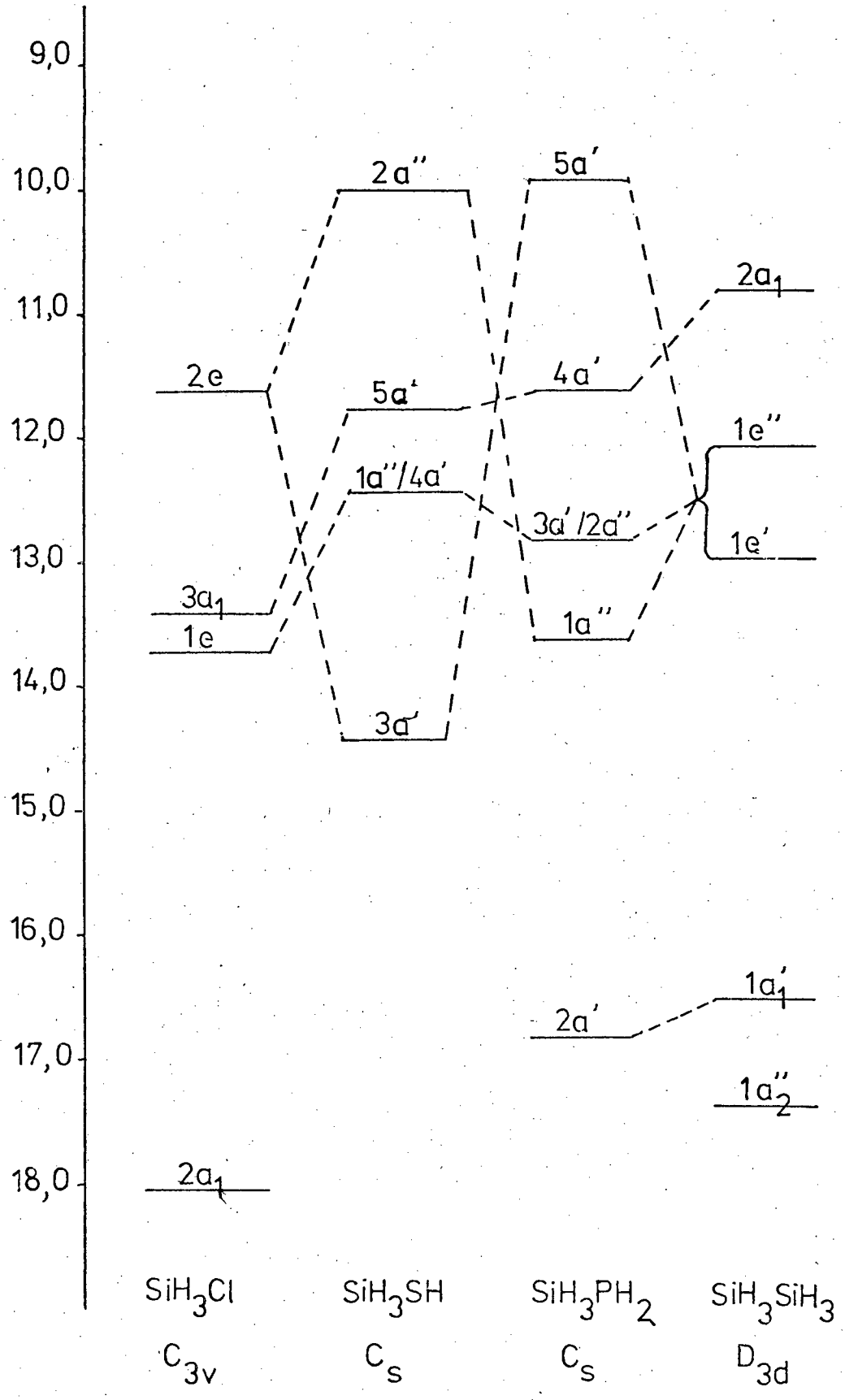
Silyl germane and silyl methane have C_{3v} symmetry, the constituent atomic and molecular orbitals being shown in table IV. The z axis lies along the Si - M bond. The only occupied classes are a_1 and e. The $3a_1$ Si - M level is formed from combination of Si and Mp_z orbitals. The $2a_1$ and $1a_1$ Si3s and Mns levels are considered as atomic orbitals, involved slightly in M - H bonding. The Si - H and M - H e bonding levels are formed by combination of the p_x and p_y orbitals on Si and M with H 1s orbitals; for sily germane and labelling is reversed. The first band is assinged to the Si - M bonding level and, in silyl methane, occurs as a shoulder, at 11.56 eV on the band due to the Si - H bonding level which is lowered by the methyl inductive effect to 11.93 eV.

The second band in methyl silane appears broadened to higher I.P. and is assigned to the $1e$ C - H σ level with Jahn-Teller splitting. The Si 3s level occurs at 16.89 eV. In silyl germane the $1e$ level

Correlation diagram I

Iso-electronic Silyl derivatives of the

2nd row elements



becomes Ge – H σ bonding and the 2e Si – H σ bonding, although in both molecules mixing may occur.

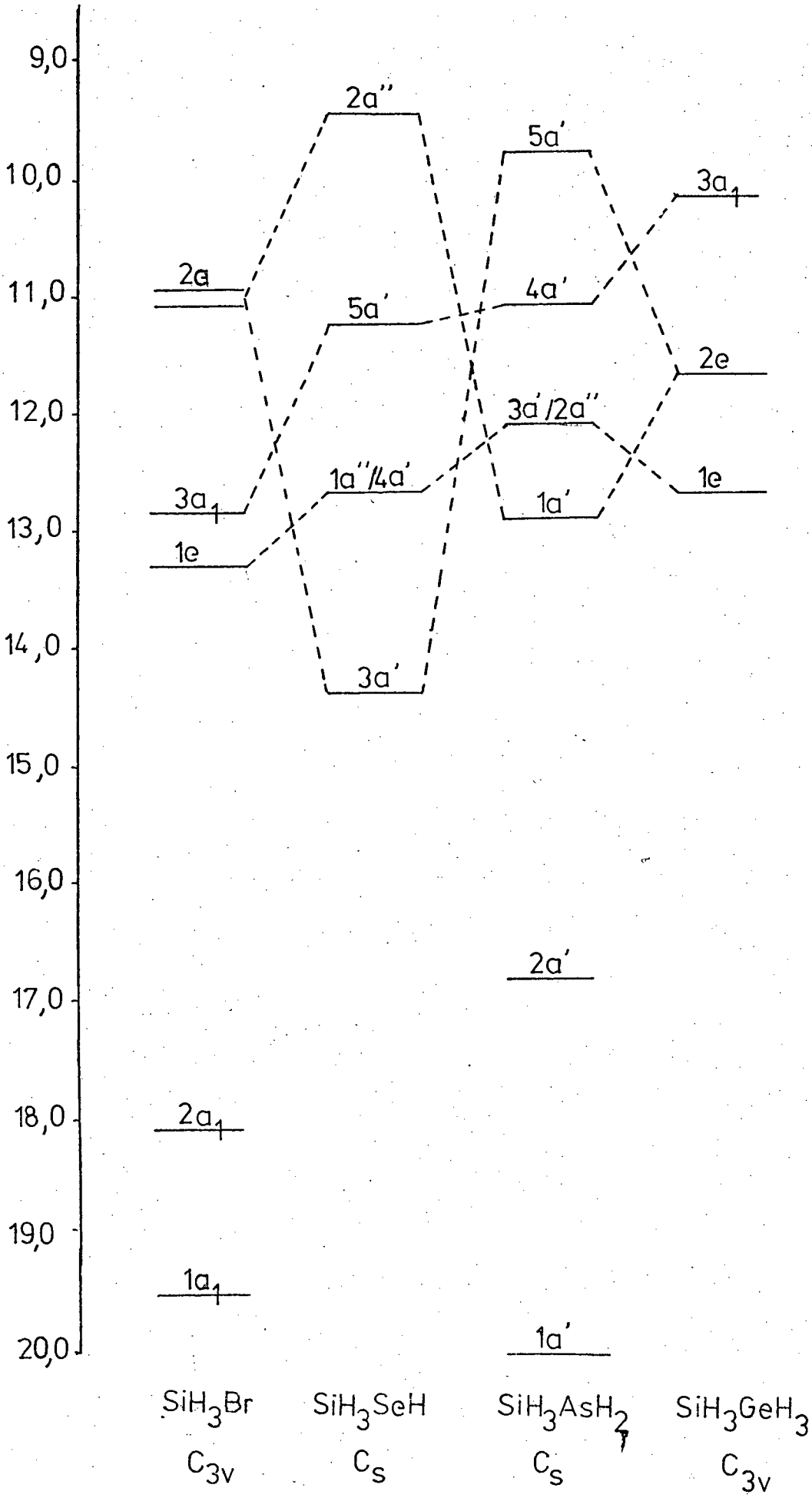
Thus the change in symmetry in the molecules produces a splitting of the degenerate e levels in the halides and group IV compounds into a' and a" components which has the effect of producing an extra bonding level at higher I.P. Similarly in the molecules of Cs symmetry, the lone-pair orbital changes symmetry from out-of-plane in Y to in-plane in Z so that the lone-pair of Sulphur or Selenium correlates in terms of symmetry although not chemically with the P – H and As – H σ levels, both being of a" symmetry. In both series the degenerate Si – H σ level decreases in energy progressively from SiH_3X to SiH_3MH_3 following the change in electro-negativity difference between Si and the substituent atom. The a' and a" components could not be resolved in SiH_3YH or SiH_3ZH_2 and the high value in silyl germane indicates interaction with the 2e Ge – H σ level. In disilane correlation must be made to both Si – H σ levels. A similar trend is found in the analogous methyl compounds.

Considering the Si – B level, (B = X, Y, Z, M), there is a similar decrease, again following the electro-negativity changes. The closeness of the 4a' Si – Z and 4a' Si – Y levels follows from the higher first I.P.s of P and As over S and Se, these levels involving p orbitals of these atoms. Thereverse situation is found in the methyl analogues, the 5a' C – P σ level being of higher I.P. than the 5a' C – S, the situation in silyl phosphine probably being due to a destabilising of the 5a' level by energetically more favourable interaction with the 4a' Si – H σ level.

On changing the silyl substituent from chlorine to a silyl group, the number of non-bonded electrons is reduced and so the amount of

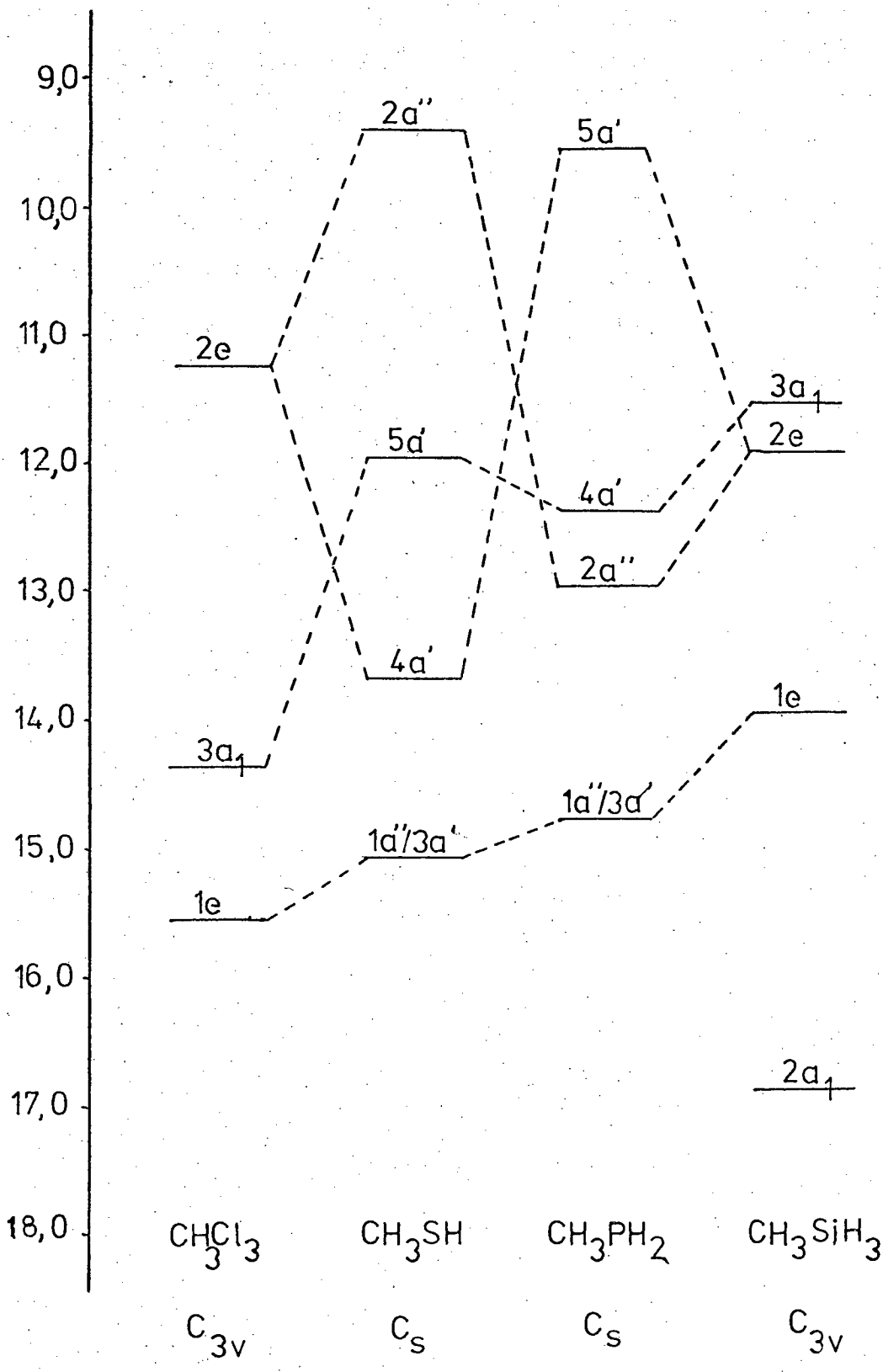
Correlation diagram II

Iso-electronic Silyl derivatives of the 3rd row elements



Correlation diagram III

Iso-electronic Methyl derivatives of the 2nd row elements



possible $(p \rightarrow d)\pi$ back-bonding will be reduced. In silyl phosphine and mercaptan, the lone-pair I.P.s are both increased from the methyl analogues, indicating $(p \rightarrow d)\pi$ bonding, but the reduction in the mercaptan is slightly greater than in the phosphine indicating greater back-bonding from S. The reverse situation occurs in the third row series the first I.P. of silyl selenol and silyl arsine following the changes in first I.P. from As to Se. The energy difference between the Se and S lone-pairs, 0.5 eV is similar to the differences in $(MH_3)_2Y$, (M = C, Si,Ge, Y = S,Se)[10] i.e. back-bonding may occur to more or less the same extent in the third row.

An interesting feature of the Y - H and Z - H σ levels is the [illegible] higher I.P.s of the Se - H and S - Ha' levels. Since the symmetry of this level changes from Y - H to Z - H this is due to more favourable interactions for Y - H a' level. A general feature of all the iso-electronic series is that as the symmetry of the molecules decreases and the molecules become smaller, the energy levels tend to be further apart. This is reflected in the stabilities of the compounds, being particularly so for sily mercaptan and silyl selenol, the latter tending to disproportionate in a matter of minutes at room temperature to give H_2Se and $(SiH_3)_2Se$.

Conclusions

The iso-electronic series are in general quite similar. $(p \rightarrow d)\pi$ bonding, which appears to be large for the halides is reduced as the number of lone-pairs available for back-bonding is reduced, there being a greater reduction in the third row than the second.

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(10) See Chapter II.

CHAPTER SIX

The Photo-electron spectra of some simple Fluorosilanes and Fluoromethanes

TABLE I

Symmetry classes of the valence shell atomic orbitals of MF_3X, (X = Cl, Br)

	a_1	a_2	e
Mns	/		
Mnp_z	/		
Mnp_x/p_y	/		/
$F2p_z$	/		/
$F2p_x/p_y$	/	/	//
Xxp_z	/		
Xxp_x/p_y			/

TABLE II

Symmetry classes of the occupied molecular orbitals of MF_3X, (X = Cl, Br)

	a_1	a_2	e
Xxp π lone-pair			4e
Si - X σ	$3a_1$		
F2p π lone-pair	$2a_1$	$1a_2$	3e 2e
Si - F σ	$1a_1$		1e

Introduction

The HeI and HeII photo-electron spectra of the series SiF_3X, ($X = H, Cl, Br, CH_3$), and the HeI spectra of CF_3X, ($X = Cl, Br,$) and Si_2F_6 were studies to see the effect of fluorine atoms on the bonding in the compounds when compared to the hydrides. The effect of the fluorine atoms on the bonding levels in a molecule, because of the high electronegativity of fluorine, is two-fold; the stabilisation of σ levels and π levels and the deshielding of the silicon atoms, by electron withdrawal, so contracting the d orbitals and making them more available for π bonding. The recently reported Perfluoro effect, the stabilisation of σ levels over π levels on substitution of H by F in planar molecules[1,2], cannot be directly applied to these molecules as the σ/π electronic distinction is destroyed by the SiF_3 group. However in hexafluoracetone and hexafluoroazomethane, where the distinction is similarly removed, the effect operates indiscriminately. Little is know on the fluorosilanes possibly due to their difficulty in preparation, a simple preparation having only recently been developed[3]. The ^{19}F N.M.R. spectra of the compounds have been run although no conclusions were drawn regarding the bonding[4]. Thus the reactions of some fluoro-silanes have been included in Appendix III.

The compounds MF_3X belong to the point group C_{3v}. The valence-shell atomic orbitals can be assigned to symmetry classes as in table I, and combine to give the occupied molecular orbitals in table II. As for the hydrides, the z axis is taken as lying along the M - X bond. There will also be Si 3d orbitals in the a_1 and e classes but not in the a_2 class. The $3a_1$ M - X σ bond is formed from the a_1 Mp_z and Xp_z atomic orbitals, the Mns again being considered separately although they may be more involved in the bonding due to delocalisation by the fluorine. The

TABLE III

Vertical Ionisation Potentials in eV. (± 0.02 eV)

	CF_3X			SiF_3X			SiF_3CH_3		Si_2F_6	
X =	Br	Cl	H (ref. 6)	Br	Cl	H				
4e	12.12	13.08		12.46	13.44		$4a_1$	13.24	$5a_{1g}$	13.20
$3a_1$	14.26	15.15	14.80	14.55	15.33	14.48	4e	14.82	$4a_{2a}/3a_{2u}$	16.24
$1a_2$	15.78	15.82	15.5	16.10	16.35	15.94	$1a_2$	15.55	$3e_g/2e_u$ $3e_u/2e_g$	17.31
3e	16.51	16.56	16.2	16.63	16.70	16.38	3e	16.25	$4a_{1g}/3a_{1g}$	17,85 (shoulder)
2e	17.42	17.53	17.24	17.36	17.49	17.24	2e	16.84	$1e_g/1e_u$	18.75
$2a_1$	19.8	20.1	19.84	18.10	18.26	18.20	$3a_1$	17.53		
1e	-	21.0	19.84	18.80	18.92	18.61	1e	18.30		
$1a_1$	-	-	24.44	20.80	20.86	20.94	$2a_1$	20.14		

TABLE IV

(a) Valence bond and (b) occupied molecular orbitals of Si_2F_6, D_{3d} symmetry

(a)

	a_{1g}	a_{1u}	a_{2g}	a_{2u}	e_g	e_u
Si 3s	/			/		
Si $3p_z$	/			/		
Si $3p_x/p_y$					/	/
F 2s	/			/	/	/
F $2p_z$	/			/	/	/
F $2p_x/p_y$	//			//	//	//

(b)

Si – Si σ	$5a_{1g}$					
F $p\pi$	$4a_{1g}$ $3a_{1g}$		$4a_{2u}$ $3a_{2u}$		$3e_g$ $2e_g$	$3e_u$ $2e_u$
Si – F σ	$2a_{1g}$		$2a_{2u}$		$1e_g$	$1e_u$
Si 3s	$1a_{1g}$		$1a_{2u}$			

Si - F σ bonds are formed from combinations of the Mnp_x/p_y a_1 and e orbitals with a_1 and e Fp_π orbitals, p_z, to give the $1a_1$ and 1e levels. The four fluorine lone-pair levels are $2a_1$, $1a_2$, 2e and 3e. The Xxp_x/p_y orbital is not involved in the bonding being the degenerate 4eX lone-pair orbitals. The relative ordering of the Si - F σ and Fp_π levels follows from the assignments for SiH_3F and SiH_2F_2. The 24 electrons needed to fill the 8 orbitals are supplied as 5 from each F and X and four from the group IV atom. In this scheme, the halogen s orbitals have been omitted as they occur at high I.P. For MF_3H the scheme is modifed; the 4e orbital disappears and the $3a_1$ becomes Si - H σ bonding. In methyltrifluorosilane, assumed to belong to the C_{3v} point group, the $3a_1$ and 4e levels become C - H σ bonding and a $4a_1$ level is introduced for the Si - C σ level. The SiF_3 σ level becomes $2a_1$ and 1e and the fluorine lone-pairs $3a_1$, $1a_2$, 3e and 2e.

The constituent atomic orbitals and valence bond orbitals for Si_2F_6 are shown in Table IV. There are combinations in all classes except a_{1u} and a_{2g}.

Spectra and Assignments

The spectra are shown in Figures (I to III) and in Correlation diagram I and the vertical ionisation potentials given in table III. Of the eight bands expected for SiF_3X and seven for SiF_3H, all are found to lie below 21.22 eV. However, the band near 21 eV was not found until the HeII spectra had been taken where it appears much stronger, due to the very low sensitivity of the instrument at that I.P. The HeII spectrum unlike the HeI involves the emission spectrum of excited Helium ions. Thus, the emission line at 584Å, (21.2 eV), is

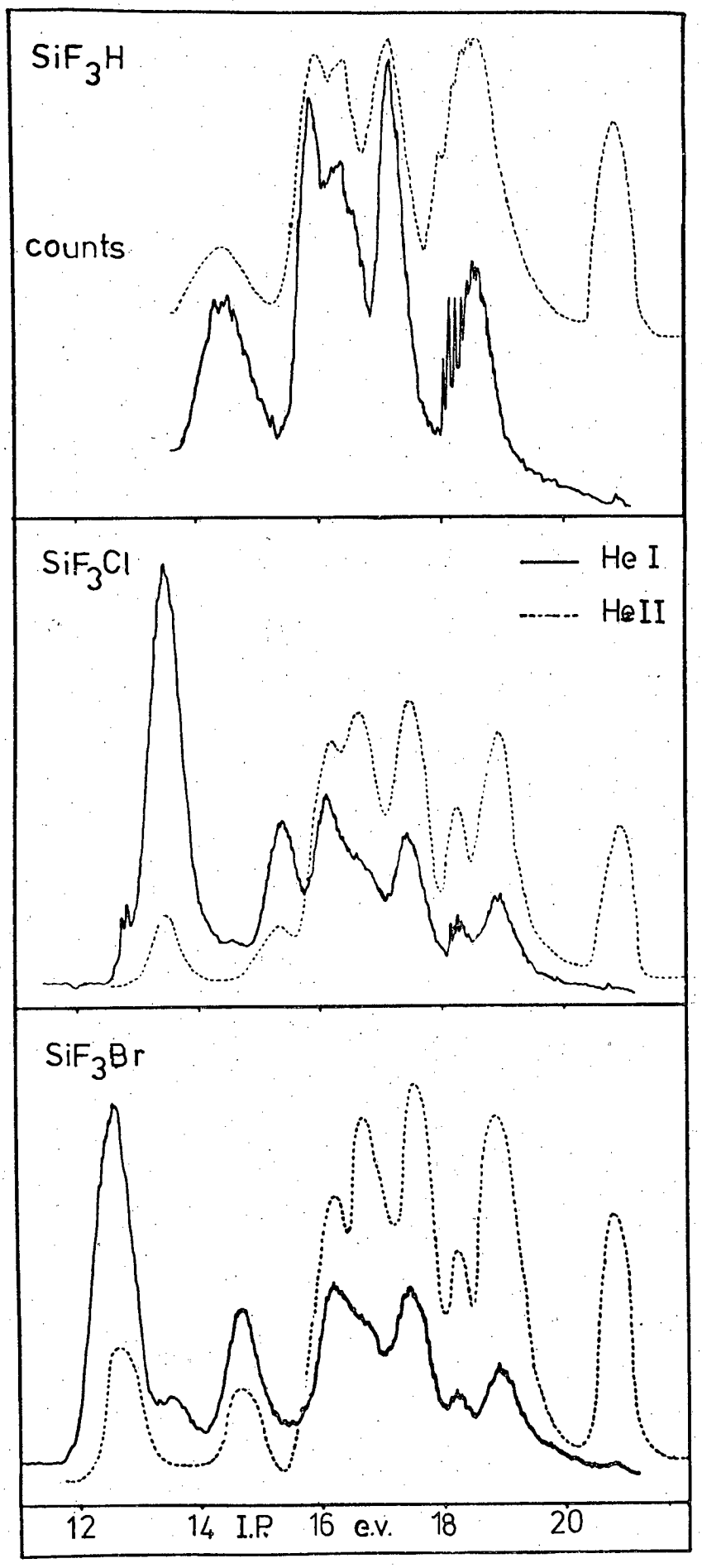


Fig I

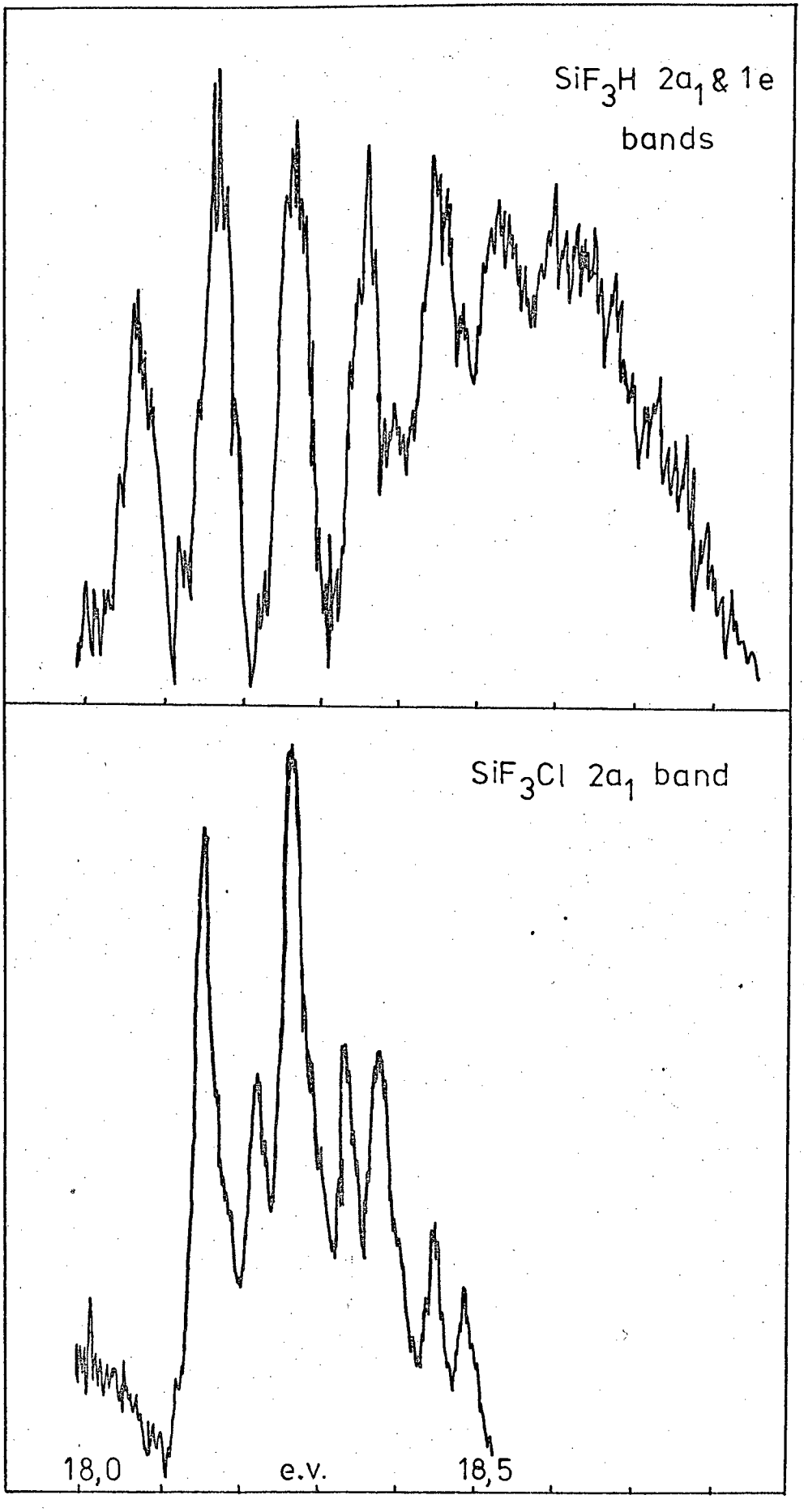


Fig Ia

produced by the change in electronic configuration of an excited He atom returning to the ground state:

$$1s^1\ 2p^1 \rightarrow 1s^2\ 2p^o$$

Also found in the spectrum of helium discharge is a line at 304A°, (40.8 eV), due to the change in configuration of an excited He ion returning to the ground state:

$$1s^o\ 2p^1 \rightarrow 1s^1\ 2p^o$$

this being the HeII line. The emission occurs at greater energy because there is no screening of the nucleus by a second electron giving a greater effective nuclear charge. However it is only a weak line. Thus using the HeII line as an ionisation source increases the energy range for ejecting electrons, i.e. of finding lower lying energy levels in the molecule. It has been postulated that as the wave-length of ionising radiation in P.E.S. is decreased, interaction of the radiation with smaller radius s orbitals becomes more favourable, the ionisation cross-section increases and the intensity of P.E. bands of s orbital origin increases relative to those from p orbitals[5].

The spectra are very similar on changing Si for C; that for CF_3H is a published one[6]. The bands have been assigned by comparison with the spectra of SiF_4[7,8] and CF_3H and with the corresponding hydrides.

In the spectra of MF_3X, the first band in each case has been assigned to the 4e Xp_π lone-pair, being intense, sharp and having a small half width which indicates lone-pair character. There is no vibrational fine structure as in the hydrides. The second band is assigned to the $3a_1$ M - X level, the separation of this level from the first being similar to that in the hydrides. In SiF_3H the first band,

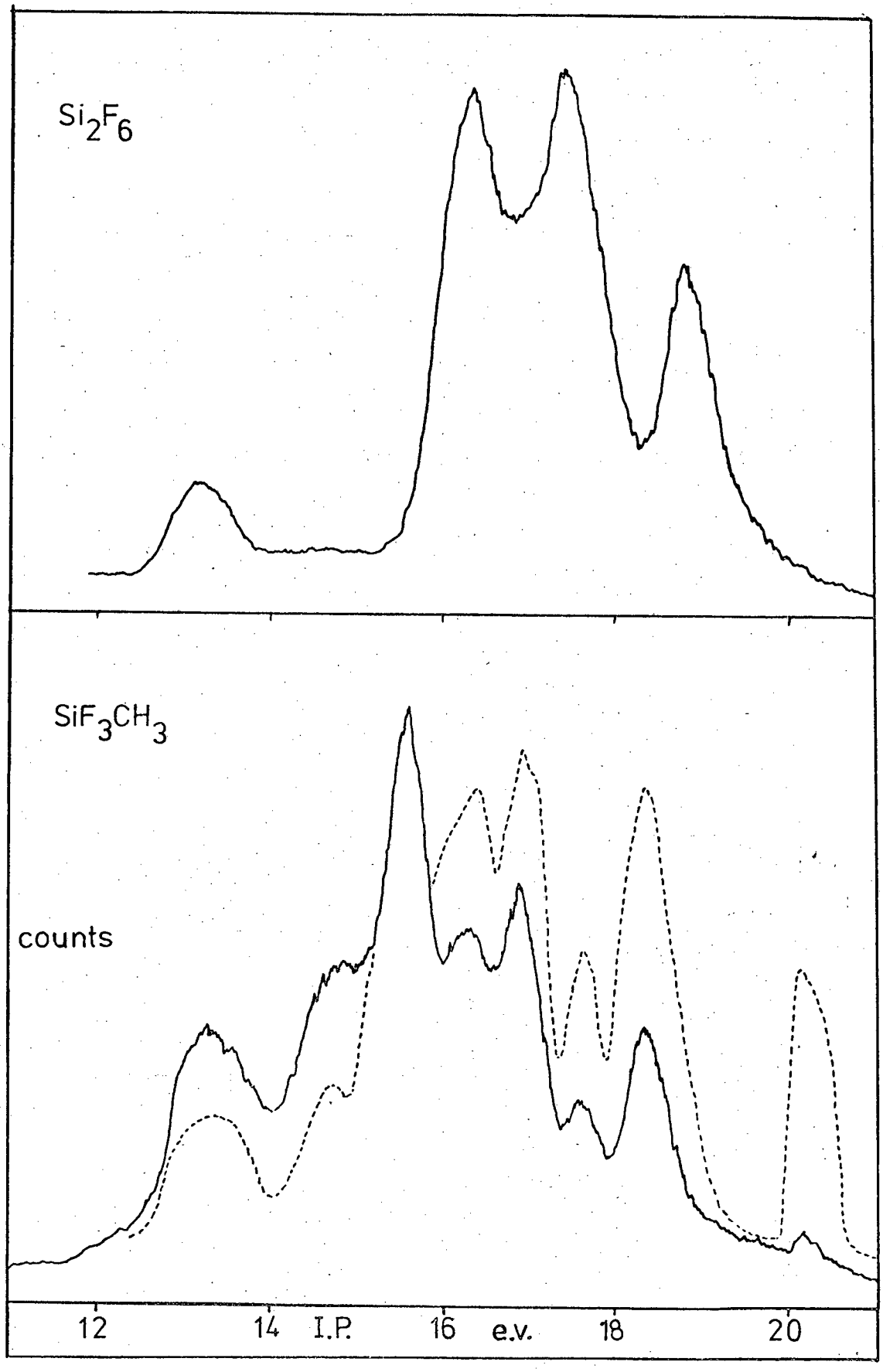


Fig II

a weak one, is assigned to the M – H $3a_1$ bonding level, as assigned and calculated for CF_3H. In methyltrifluorosilane the first two bands are assigned to the 4e and 4a, C – H and Si – C σ bonding levels respectively. The next three bands in all the compounds are assigned in order of increasing I.P. to the $1a_2$, 3e and 2e Fp π lone-pair orbitals, the $1a_2$ occuring at lowest I.P. as it is the combination of atomic orbitals with no overlap and so has slight anti-bonding character. In CF_3X the 2e level shows reduced CF_3 stretching and deformation frequencies, as shown in table IV, this being consistent with the spectrum of CF_3H. The $1a_1$ band in these compounds is expected to lie above 21.2 eV by analogy with CF_3H[6]. The band at 20.5 eV in CF_3H, assigned to the $2a_1$ and 1e levels, splits into two bands in CF_3Cl at 20.15 and 21.0 eV and one in CF_3Br at 19.8 eV. The bands at 20.15 and 19.8 eV in the chloride and bromide respectively show vibrational progressions assigned to reduced CF_3 deformation modes, these being of a_1 symmetry. Since the reduction from the ground state frequency varies with the size and weight of the substituent halogen, the ejected electrons would appear to be skeletal bonding and not fluorine p_π lone-pair. The band is thus assigned to the $2a_1$ level.

Considering the remaining three bands in the silane two, those near 18 eV and 21 eV show fine structure, shown in table IV. The band at 21 eV show two progressions with spacings indicating the excitation of SiF_3 stretching and deformation frequencies in the molecular ion SiF_3X^+. The band at 18 eV shows one progression in a reduced Si – F stretching frequency except for the chloride where increased Si – Cl and Si – F stretching frequency are found. Since only an a_1 symmetric vibration

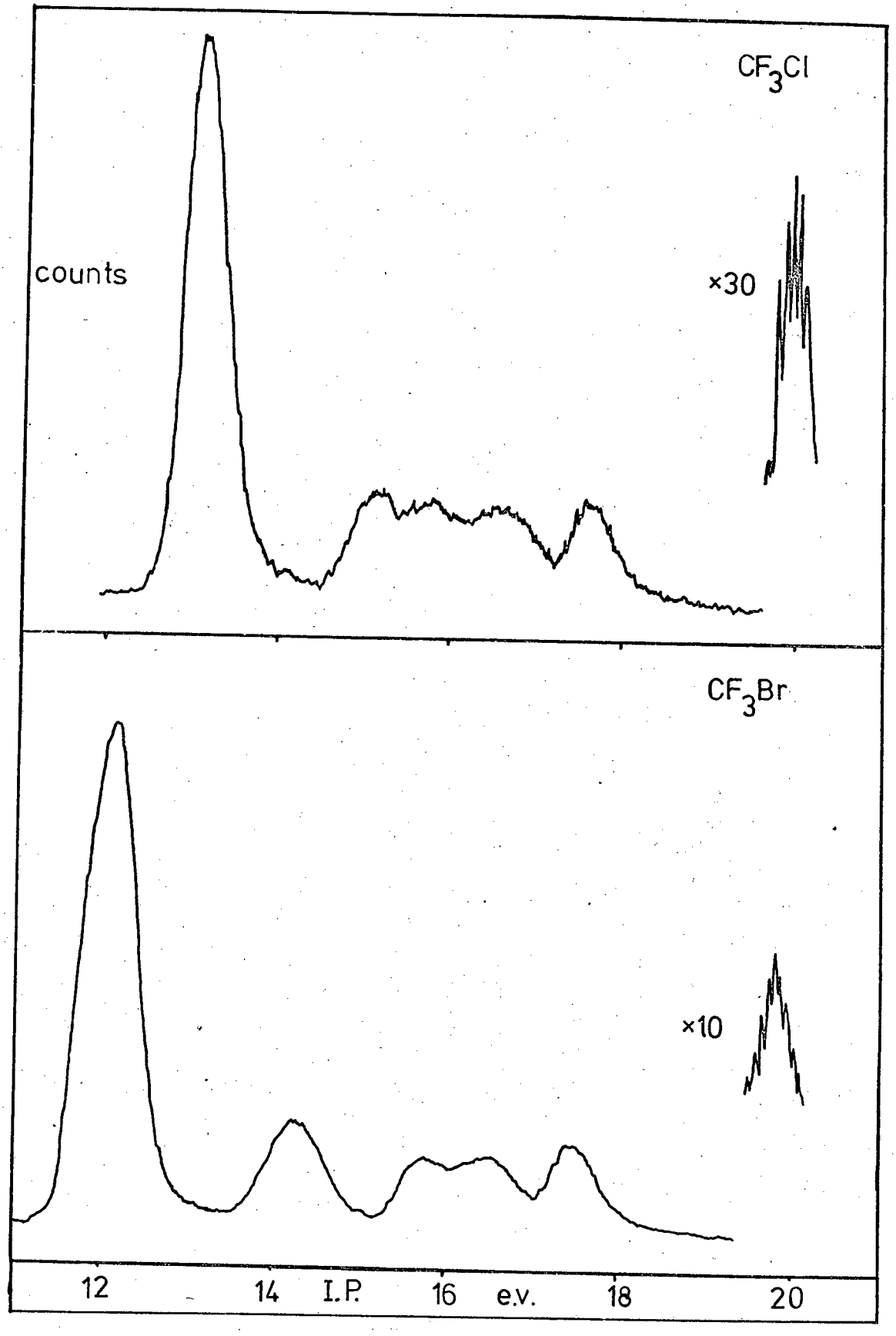


Fig III

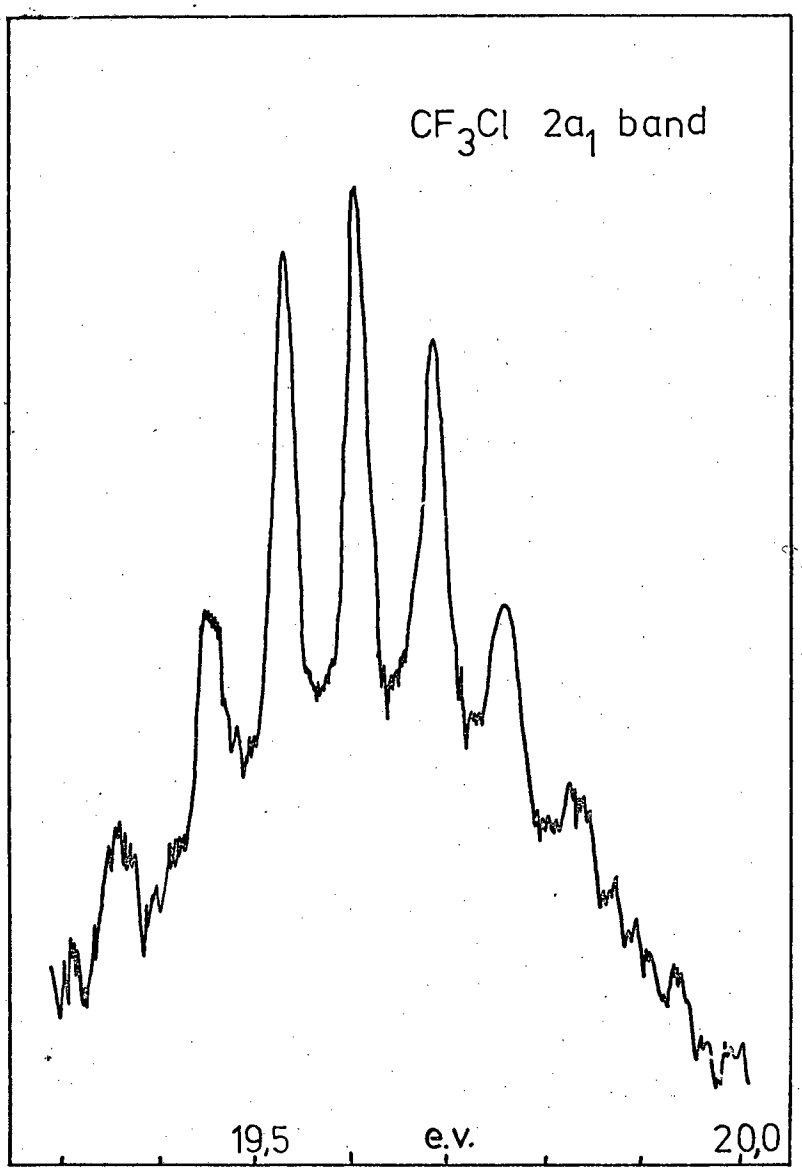


Fig IIIa

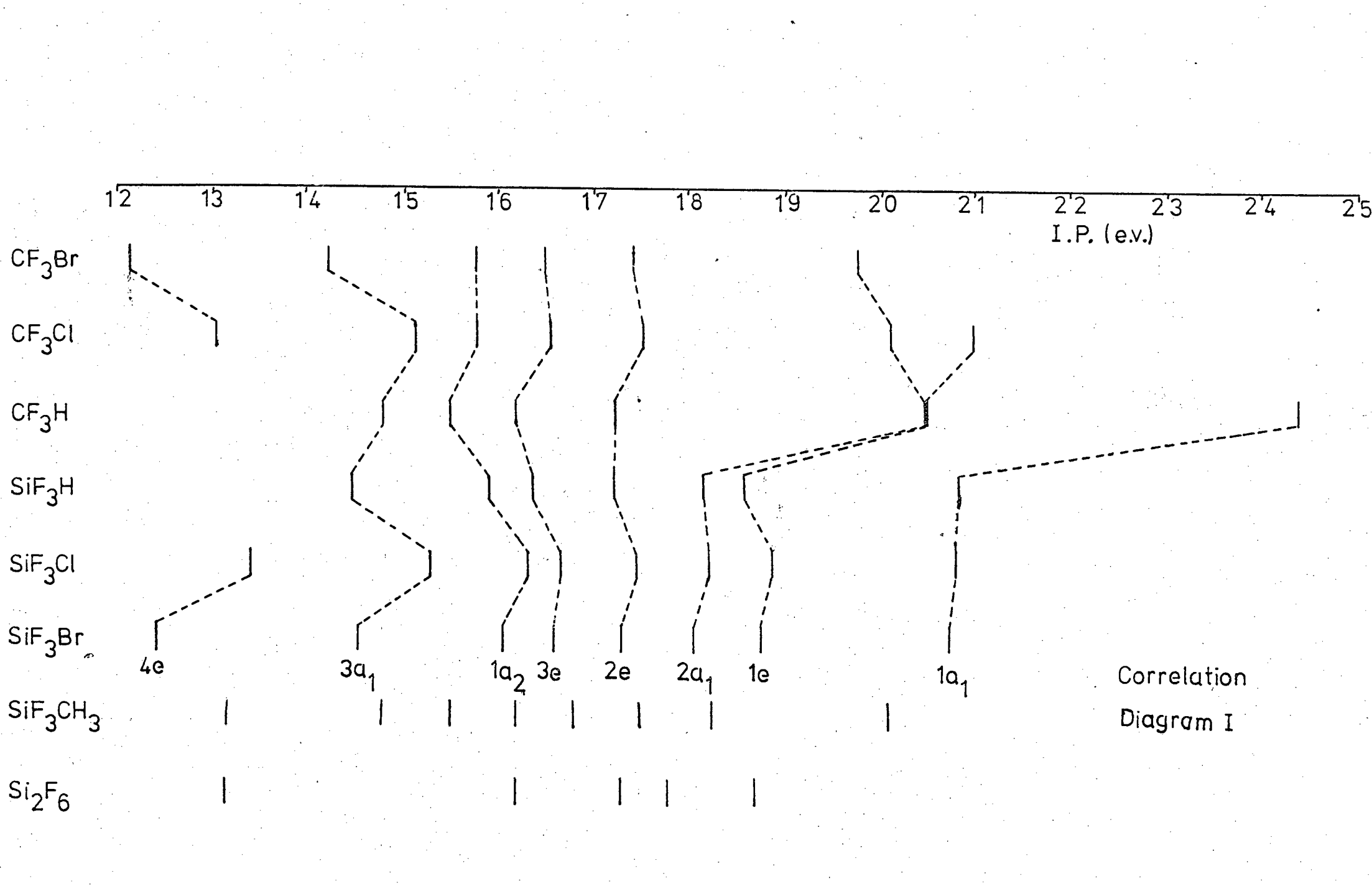
can be excited, the increased frequencies may indicate slight anti-bonding. character in this level. The two bands are assigned to mixtures of the $1a_1$ Si - F σ and $2a_1$ Fp π lone-pair levels, the Si 3s being mainly on the $1a_1$ level at 21 eV. The HeII spectra show a large increase in intensity of this band. It has been suggested [15] that levels with mainly s character are increased in intensity on changing from HeI to HeII radiation. However, in view of the fall-off in detector sensitivity for low energy electrons, no correlation can be made. For Si_2F_6 the first weak band is assigned to the $5a_{1g}$ Si - Si σ bonding level. The next three bands, of higher intensity are assigned in order of increasing I.P. to the $4a_{2u}/3a_{2u}$, $3e_g/2e_g/3e_u/2e_u$, $4a_{1g}/3a_{1g}$. The latter occurs as a shoulder but is expected to be weak by correlation to the $2a_1$ level in the SiF_3 compounds and the e level in SiF_4, (8), which are also weak. The fifth band at 18.75 eV is assigned to the $1e_g$ and $1e_u$ Si - F bonding levels, correlating well with the 1e level in SiF_3X. The band corresponding to the $1a_1$ level in SiF_3X is assumed to lie beyond 21.2 eV as for SiF_4.

As stated the effect of fluorine atoms on the bonding of the molecules is to increase the possibility of $(p \rightarrow d)\pi$ bonding and to stabilise levels. Also there is the possibility of $(p \rightarrow d)\pi$ bonding between the fluorine atoms and the silicon. As for the hydrides the I.P. of the p_π electrons on X attached to silicon is greater than that on the corresponding carbon compounds. Since the electro-negativities are of the order C > Si, this stabilisation may be explained by $(p \rightarrow d)\pi$ bonding. The band contours indicate that the lone-pairs are not strictly non-bonding as in methyl halides, but no fine structure is found on any of the 4e level bands as in the hydrides. There is also the possibility that

interaction could occur with M – F anti-bonding levels as suggested by the excited virbrations. It has been suggested from the spectra of acetone and hexafluoroacetone that in the latter, the lone-pair on the oxygen is delocalised over the fluorine atoms. The lone-pair electrons in the carbon compounds are not strictly non-bonding by consideration of their band shapes, possibly as a result of a similar delocalisation, which would lower the level. This lowering could also be due to interaction with other e levels, Fp_{π} and C – Fσ , a large interaction raising the 4e level and lowering the 1e.

The effect of the fluorine atoms on the σ levels is shown in table V, comparing the spectra of the fluorides to the hydrides. For carbon, the effect of substitution F for H is to stabilise the 4e π level more than the $3a_1$ σ level by a factor of about 2.

For the silicon compounds the situation is reversed and the σ level is stabilised more than the π level, the stabilisation occuring to such an extent that the Si – Cl bond becomes stronger than the C – Cl bond. Thus the bonding between M and X is not simple. The large σ acceptor ability of the SiF_3 group could be a large factor causing polarisation, shortening and so strengthening of the Si – X bond. This is observed in other compounds; in the series of transition metal complexes $SiX_3Mn(CO)_5$, (X = Me, H, Cl, F), the I.P. of the Si – Mn σ bond changes from 9.3 eV to 9.0 to 9.3 to 10.4 eV for X = Me, H, Cl, F respectively while the I.P.s of the manganese d orbitals stay relatively constant[13]. The I.P.s of the σ levels in SiF_3Me, Si_2F_6 and some related compounds are shown in table VI. Again on substitution of fluorine for hydrogen the I.P. increases dramatically; this is not so for chlorine, possible due to its lower eleotro-negativity.


12
13
14
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16
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18
19
20
21
22
23
24
25
I.P. (e.v.)
CF3Br
CF3Cl
CF3H
SiF3H
SiF3Cl
SiF3Br
SiF3CH3
Si2F6
4e
3a1
1a2
3e
2e
2a1
1e
1a1
Correlation
Diagram I

The I.P.s of the Fp_π electrons are found to be slightly higher for the silicon than the carbon compounds, possibly due to $(p \rightarrow d)\pi$ bonding as has been postulated for SiF_4[7]. The I.P.s are relatively constant despite variation in the elctron withdrawing or accepting ability of X in SiF_3X, although there is a slight shift to lower I.P. with a methyl substituent. The constancy is possible the result of the very high electro-negativity of fluorine, σ/π mixing between M – F σ levels and Fp_π levels having little effect on the I.P.s and any $(p \rightarrow d)\pi$ back-bonding being opposed by electron release from silicon. However, the $1a_2$ Fp_π lone-pair occur at higher I.P. in SiF_3X than in CF_3X but there are no d orbitals of a_2 symmetry for any $(p \rightarrow d)\pi$ interaction to occur. Thus again interaction with Si – F σ^* orbitals may be postulated. A similar constancy of Fp_π levels is found in the series BF_3, CHF_3, NF_3, PF_3 and AsF_3 where the a_2', e' and e" levels are quite constant[14]. When electron withdrawing bromine is replaced by a methyl group all the Si – F σ and Fp_π levels are shifted to lower I.P. from the bromide by an amount between 0.4 and 0.55 eV. However the $2a_1$ level in methyl-trifluorosilane, corresponding to the $1a_1$ in SiF_3X is shifted by 0.65 eV showing that the Si 3s may be involved in the Si – C bonding since the shift of the 3s level from silane to methylsilane is $\sim$ 1.2 eV, this probably being due to the inductive effect of the methyl groups.

Various interpretations of the spectrum of SiF_4 have been made[8,7,5], but it is generally agreed that the first three bands are assigned to the t_1, t_2 and e fluorine lone-pairs at 16.45, 17.53 and 18.11 eV and the last two to the t_2 and a_1 Si – F σ levels at 19.51 and 21.7 eV. The spectrum of CF_4 is very similar, the lone-pair levels occuring at

16.20, 17.40 and 18.50 eV. One large difference in SiF_3X is the lowering of the I.P. of Si 3s level from SiF_4 at 21.7 eV by about 1.0 eV, this showing decreased bonding character similar to the lowering of this level in SiF_3Me. Thus agreement with the assignments made here is good.

Conclusions

The assignments for the P.E. spectra of the compounds SiF_3X (X = SiF_3, Me, H, Cl, Br) indicate no direct evidence for (p → d) π bonding between X, (Cl, Br), and Si. The assignments correlate well with the carbon analogues and also with CF_4 and SiF_4. Due to the high electro-negativity of the fluorine atoms, the SiF_3 group has a large effect on the Si - X σ-bonding levels. However, the bonding between silicon and fluorine and between silicon and the other substituent atoms cannot be described simply.

TABLE IV

Vibrational progressions excited in the $1a_1$ and $2a_1$ levels of SiF_3X, (X = H, Cl, Br, CH_3) and in the 2e and $2a_1$ levels of CF_3X, (X = H, Cl, Br). Values are quoted to ± 40 cm^{-1}

	$2a_1$	$1a_1$	Molecular vibration frequencies		Reference
SiF_3H	790	725 330	998 858 425	ν Si – F δ SiF_3	(9)
SiF_3Cl	965 605	890 260	1000 880 596 345	ν Si – F ν Si – Cl δ SiF_3	(15)
SiF_3Br	850	755 240	1000 867 330	ν Si – F δ SiF_3	(15)
SiF_3Me	730	845 325	980 900 392	ν Si – F δ SiF_3	(12)
	2e	$2a_1$			
CF_3H	1050 500	– –	1117 1152 697	ν C – F δ CF_3	(6)
CF_3Cl	1130 725	630	1210 1102 783	ν C – F δ CF_3	(10)
CF_3Br	1020	485	1188 1067 760	ν C – F δ CF_3	(11)

TABLE V

Vertical ionisation potentials (± 0.02 eV) of MH_3X, (M = Si, C, Y = F, H, X = Cl, Br)

	SiH_3X	SiF_3X	CH_3X	CF_3X
Cl p_π lone-pair	11.61	13.44	11.28	13.08
M – Cl σ	13.4	15.33	14.4	15.15
Br p_π lone-pair	10.96	12.46	10.53	12.12
M – Br σ	12.85	14.55	13.5	14.26

TABLE VI

Vertical ionisation potentials of the highest a levels of SiF_3Me, Si_2F_6 and some related compounds, (± 0.02 eV)

	SiF_3CH_3	SiH_3CH_3		
Si – C σ	13.24	11.56		
	Si_2Me_6	Si_2H_6	Si_2Cl_6	Si_2F_6
Si – Si σ		10.7	10.8	13.2

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(15) Observed Assignments.

APPENDICES

Appendix I

The Determination of the structures of Silacyclopent-3-ene and its 1:1 dichloro derivative

The structures were determined in the gas phase by the electron diffraction technique. This makes use of the property of electrons of being diffracted by pairs of atoms as light is by a narrow slit. The diffraction patters for each species were recorded photographically, by Dr. D. W. H. Rankin using the Balzers KD 62 gas diffraction apparatus at the Manchester Institute of Science and Technology. Three plates were exposed for each sample at nozzle-to-plate distances of 250, 500 and 1,000 mm. The intensity information on the plates was converted to digital form using a fully automated Joyce-Loebl microdensitometer at the Royal Observatory, Edinburgh. Reduction of the data and least squares refinements were performed on an I.B.M. 350/60 computer at the Edinburgh Regional Computing Centre.

The programmes used were very similar to those previously desribed by G. M. Sheldrick et al[1] and work in four stages.

The first stage combined the corrected traces and subtracted a calculated atomic scattering curve. A cubic curve was then subtracted to level the data across the plate.

The second stage entailed the subtraction of a background curve to account for incoherent atomic scattering and other extraneous scatterings. The best curve was found in both cases by comparison of the data from all three plates, a line being drawn to obtain a simusoidal curve.

The third stage was aleast squares refinement programme based on

that of Hedberg[2]. The complex scattering factors of Cox and Bonham were used[3]. The data found experimentally were compared to the diffraction pattern based on a model of the compound. Two R factors, measures of the agreement between the experimental and theoretical structures were calculated:

$$R_g = \left(\frac{\bar{U} W U}{\bar{I} W I} \right)^{\frac{1}{2}}$$

and

$$R_d = \left(\frac{\Sigma w_{jj} U_j^2}{\Sigma w_{jj} I_j^2} \right)^{\frac{1}{2}}$$

where I = vector of intensities, U = vector of residuals and w = weight matrix with elements w_{jk}.

The final stage of the programme calculated and plotted the radial distribution curves. The distances calculated in the refinement stage correspond to the centres of gravity of the peaks in the P(r)/r curve.

The wavelength associated with the electron beam used to produce the diffraction patterns was measured from the pattern given by a sample of powdered thallous chloride and was found to be 0,05663 Å, ($\pm$ 0.00003 Å).

The molecular model used in the refinement assumed C_{2v} symmetry, this being indicated by low frequency I.R. studies[4]. The ring was also assumed planar and the hydrogens at the double bond as bisecting the C—C=C ring angle. Independent parameters were the five bonded distances Si - C, C - C, C = C, C - H and Si - X, (X = H, Cl), and the angles X-$\hat{\text{Si}}$-X, H-$\hat{\text{C}}$-H and C-$\hat{\text{C}}$=C which defined the model. All the C - H distances were considered the same length. Other independent parameters were the three scale factors and the amplitudes of vibration of four independent and twenty dependent distances in the hydride and of three independent and nineteen dependent distances in the chloride. The

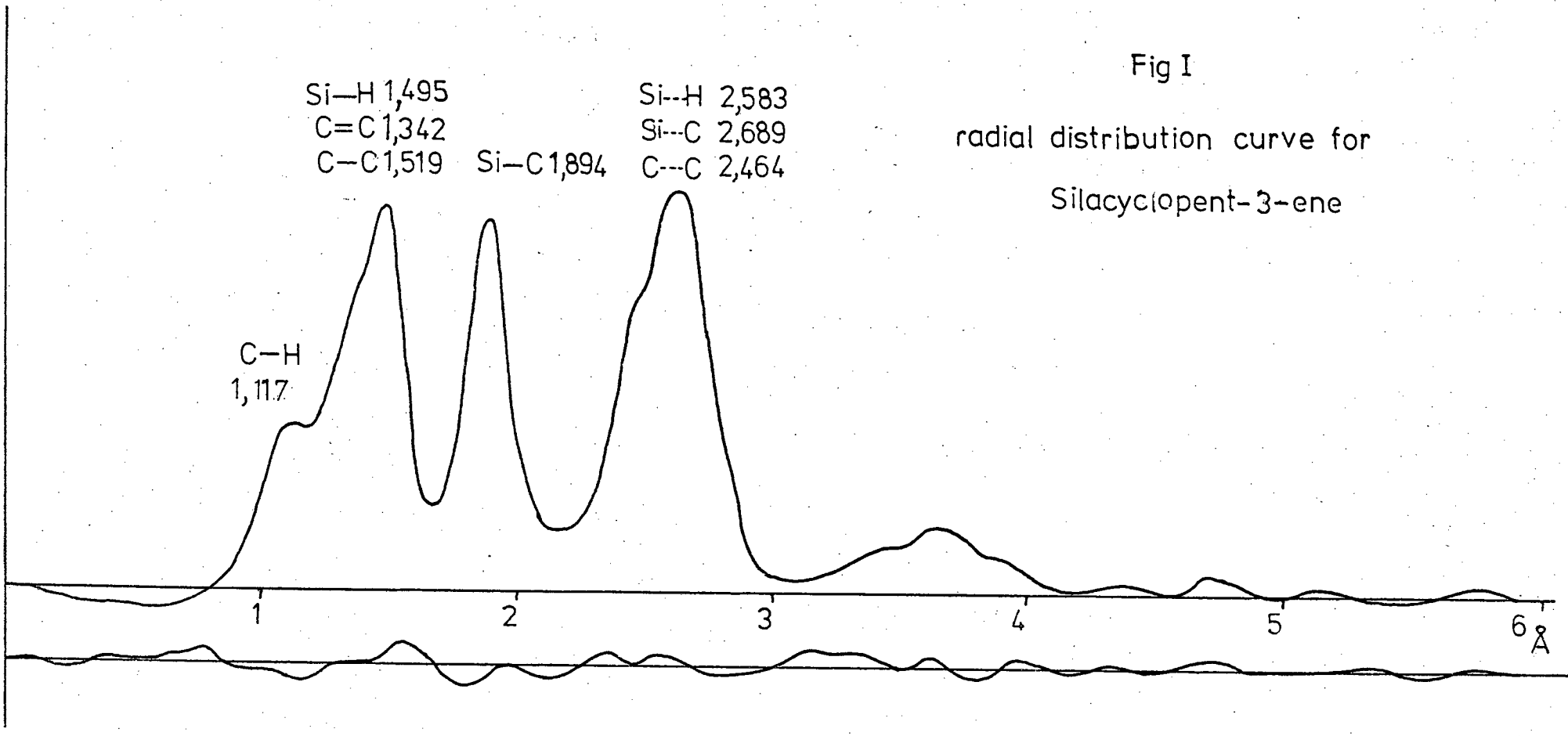


Fig I

radial distribution curve for

Silacyclopent-3-ene

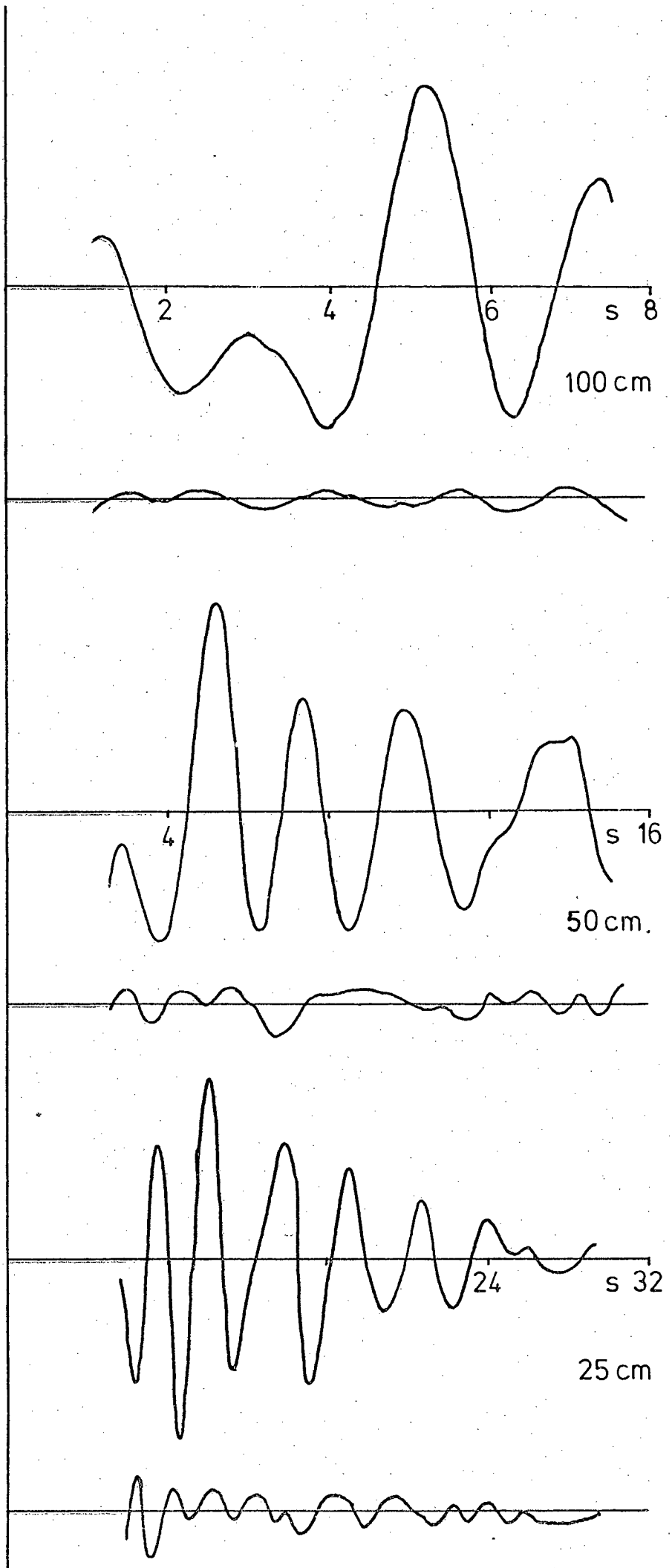


Fig II Intensity data for $SiH_2C_4H_6$

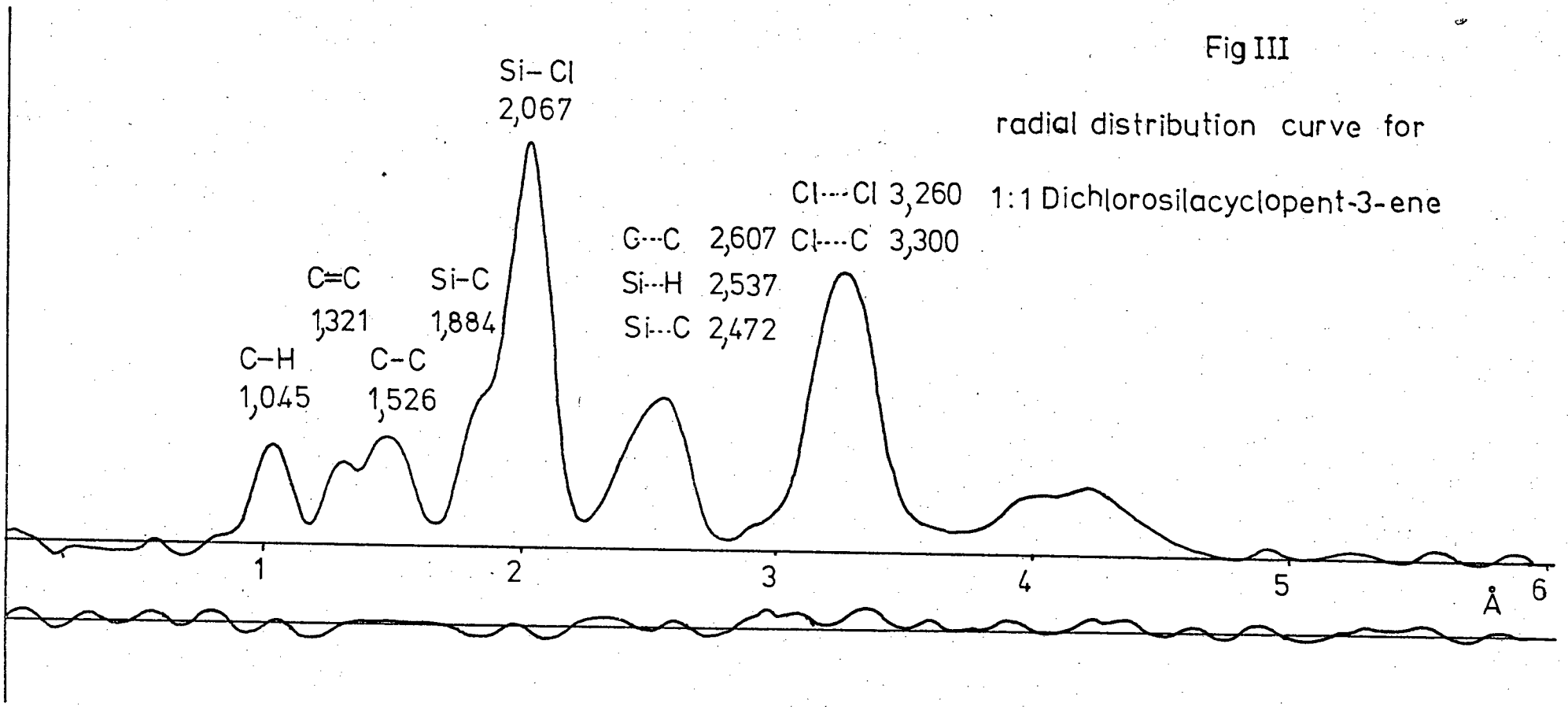


Fig III

radial distribution curve for

1:1 Dichlorosilacyclopent-3-ene

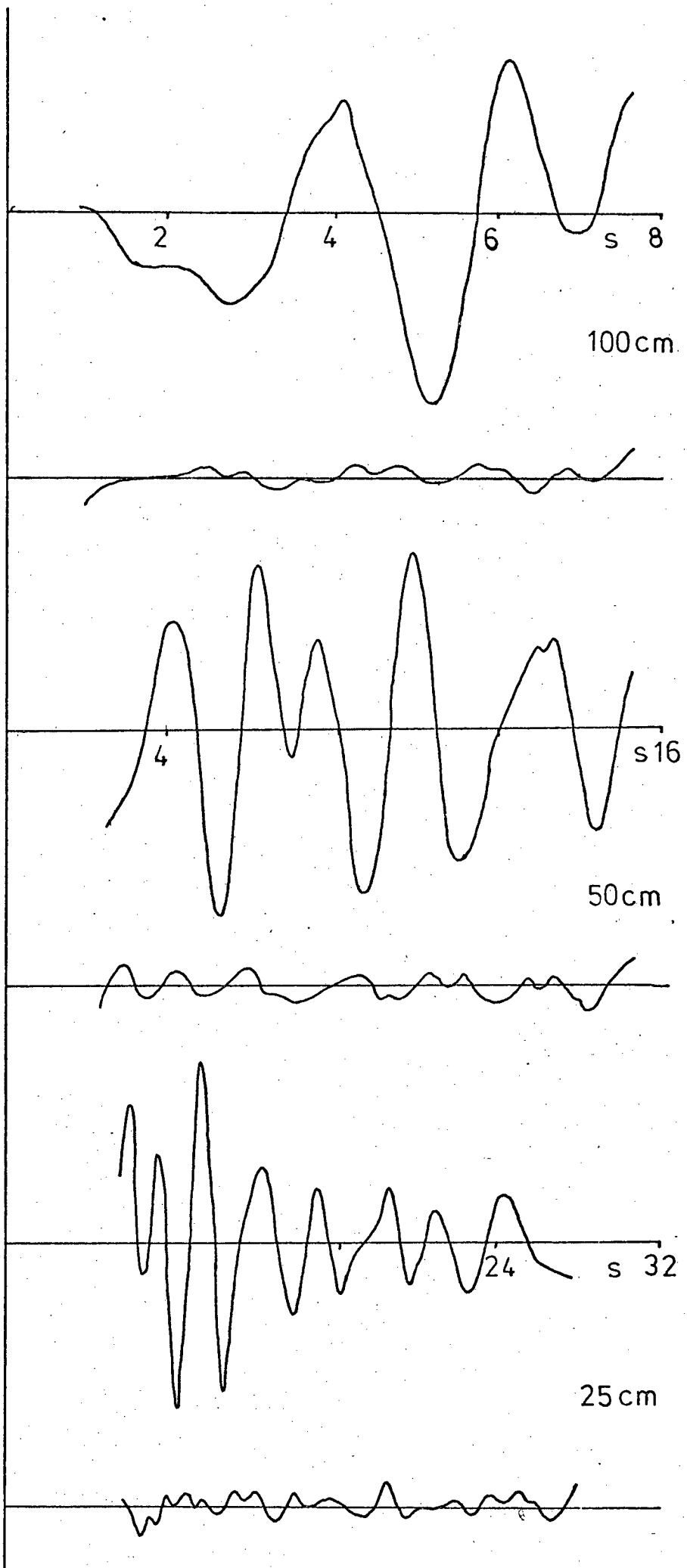


Fig IV Intensity data for $SiCl_2C_4H_6$

intensity data, radial distribution curves and structures are shown in Figures I to V and the molecular and experimental parameters in tables I to IV.

Silacyclopent-e-ene

It was found necessary to fix the Si - H bond length near 1,5 Å and the refining independent amplitude of vibration was that of the (C - C) bond. The two angles H-$\hat{Si}$-H and H-$\hat{C}$-H were also fixed near the tetrahedral angle. The amplitude of the long (C---C) distance was allowed to refine, the amplitude of the short (C----C) distance being constrained to be equal to it. The amplitude of the trans-annular (C----H) distance was allowed to refine, the amplitudes of the other two (C----H) distances being constrained to be equal to it. The radial distribution curve showed a slight separation of the non-bonded carbon-carbon distances and of the non-bonded carbon-hydrogen distances.

This led to an R factor of 0,19,(R_g), or 0,12,(R_d). This was rather large but in view of the low frequency bending vibration of the ring there could be considerable differences between real and apparent trans-annular distances - the apparent shrinking effect[5].

Initial refinements incorporating a modifed model allowing the silicon to move out of the plane of the carbon atoms has led to a slight reduction in the R. factor. A minimum of 0.175 was found with a bending angle of 6°. As the molecule has a very low energy barrier to ring inversion[4] this is thought to be a shrinkage effect.

1:1 Dichlorosilacyclopent-3-ene

Here it was again found necessary to fix the H-$\hat{C}$-H and Cl-$\hat{Si}$-Cl bond angles near the tetrahedral angle but the (Si - Cl) bond length was allowed to refine. The (Si - Cl) amplitude was allowed to refine and

aonstraining the (Si - C) amplitude to be equal to it lead to a slight separation of peaks in the radial distribution curve. Refining the (C - C) amplitude led to a separation of the peak from the (C = C) bond. Refinement of the (Cl·····Cl) amplitude with the (C····Cl) amplitude being constrained to id did not produce any separation in the peak near 3,2 Å.

Under these conditions the R factor was found to reduce to 0,17,(R_g) or 0,12,(R_d), again being rather large. Using the modified model has served only to raise the R factor two or three fold with a bending angle of 4.

Thus the chloride appears to be more distorted from a regular pentagon than the hydride. This could be a result of σ electron withdrawal by the chlorine, decreasing electron pair repulsions or increasing the possibility of ($\pi \rightarrow d)\pi$ bonding across the ring. Thus the structure of the fluoride should prove interesting.

TABLE I

Weighting functions, Correlation parameters and Scale factors for Silacyclopent-3-ene

Height	Del S	S Min	S1	S2	S Max	P/H	Scale factor	Wavelength
250.0380	0.400	6.000	11,000	15.000	19.600	0.3997	0.775 ± 0.016	0.05663
500.0579	0.200	2.800	4.500	13.000	15.400	0.4930	0.680 ± 0.015	0.05663
1000.0618	0.100	1.200	2.200	6.300	7.700	0.4938	0.624 ± 0.023	0.05663

Weighting functions, Correlation paramters and Scale factors for 1:1 Dichlorosilacyclopent-3-ene

Height	Del S	S Min	S1	S2	S Max	P/H	Scale factor	Wavelength
250.0380	0.400	6.000	8,800	25.200	28.500	0.4078	1.209 ± 0.039	0.05663
500.0576	0.200	2.600	4.200	12.500	15.400	0.4741	1.137 ± 0.030	0.05663
1000.0615	0.100	1.000	2.000	6.500	7.800	0.4819	1.061 ± 0.043	0.05663

TABLE II

Least Squares correlation matrices multiplied by 1000

(a) Silacyclopent-3-ene

R11	R 2	R 3	R 5	< 1	U 2	U 7	U15	K 1	K 2	K 3
1000	441	471	-32	-809	-178	-77	-138	-280	-285	-224
	1000	270	7	-579	-38	0	45	6	-120	-129
		1000	49	-243	-187	-129	-642	-229	-287	-328
			1000	148	-32	30	-25	-164	-28	68
				1000	132	-25	-164	201	131	113
					1000	29	86	383	116	88
						1000	95	19	212	147
							1000	114	22862	233
								1000	139	78
									1000	123
										1000

(b) 1:1 Dichlorosilacyclopent-3-ene

R 1	R 2	R 3	R 4	R 5	< 1	U 2	U 4	U 6	U 7	U15	K 1	K 2	K 3
1000	121	213	345	630	-424	-107	-42	-170	9	-178	-207	-104	102
	1000	-19	190	276	-177	1	91	69	31	-408	48	104	134
		1000	-16	80	-101	-111	13	19	214	-156	-20	205	181
			1000	-11	-523	-4	192	216	52	-239	248	234	91
				1000	-213	-72	-138	-360	-71	-357	-358	-251	45
					1000	31	-276	-284	-68	557	-314	-300	-164
						1000	-53	58	-9	19	92	28	-50
							1000	515	169	-179	679	488	181
								1000	169	-107	711	570	201
									1000	-61	202	245	173
										1000	-127	-211	179
											1000	519	162
												1000	178
													1000

TABLE III

Molecular papameters for silacyclopent-3-ene

Independent distances (Å)		Amplitudes (Å)
r 1 (C ≠ C)	1.344 ± 0.006	0.045 (fixed)
r 2 (C – C)	1.519 ± 0.003	0.049 ± 0.004
r 3 (C – H)	1.117 ± 0.007	0.090 (fixed)
r 4 (Si – H)	1.495 (fixed)	0.065 (fixed)
r 5 (Si – C)	1.894 ± 0.002	0.059 (fixed)
Dependent distances		
d 1 (H...H)	2.419 ± 0.005	0.220 (fixed)
d 2 (H...C)	3.747 ± 0.013	0.239 ± 0.025
d 3 (H...C)	2.838 ± 0.007	0.130 (fixed)
d 4 (H...H)	4.769 ± 0.019	0.200 (fixed)
d 5 (H...H)	2.993 ± 0.007	0.130 (fixed)
d 6 (H...H)	3.652 ± 0.012	0.150 (fixed)
d 7 (Si...C)	2.688 ± 0.013	0.068 (fixed)
d 8 (Si...H)	3.774 ± 0.018	0.150 (fixed)
d 9 (Si...H)	2.584 ± 0.007	0.033 (fixed)
d10 (C...C)	2.807 ± 0.006	0.049 ± 0.006
d11 (C...C)	2.466 ± 0.006	0.049 (tied to U15)
d12 (C...H)	3.579 ± 0.009	0.239 (tied to U 7)
d13 (C...H)	2.299 ± 0.012	0.130 (fixed)
d14 (C...H)	3.500 ± 0.013	0.239 (tied to U 7)
d15 (C...H)	2.125 ± 0.007	0.130 (fixed)
d16 (C...H)	2.141 ± 0.012	0.130 (fixed)
d17 (H...H)	4.499 ± 0.014	0.200 (fixed)
d18 (H...H)	4.120 ± 0.011	0.200 (fixed)
d19 (H...H)	4.120 ± 0.016	0.200 (fixed)
d20 (H...H)	2.597 ± 0.012	0.120 (fixed)
d21 (H...H)	2.482 ± 0.016	0.150 (fixed)
d22 (H...H)	1.808 ± 0.011	0.220 (fixed)

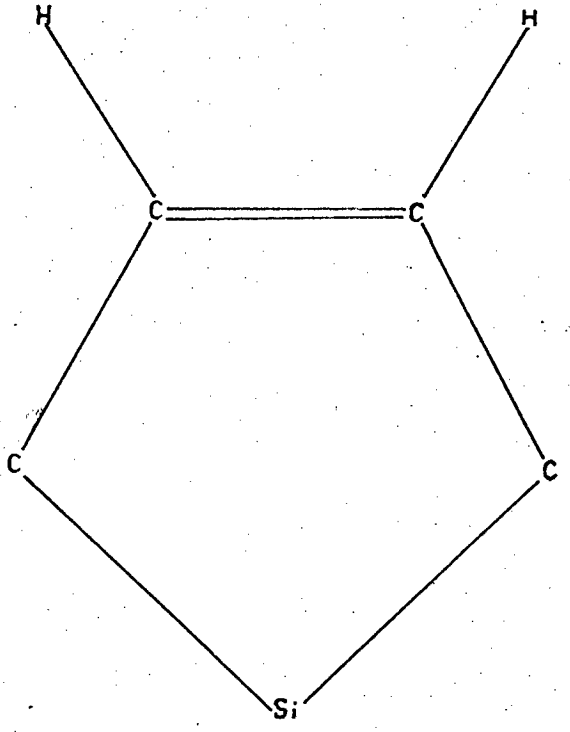
Table III (continued)

Independent Angles

1 (C ≑ C – C)	118.77 ± 0.22
2 (H – Si – H)	108.00 (fixed)
3 (H – C – H)	108.00 (fixed)
4 (tilt)	0.000 (fixed)

Dependent angles

5 (C – Si – C)	95.67
6 (Si – C – C)	103.39



1" : 1 Å

Fig V

TABLE IV

Molecular paramters for 1:1 dichlorosilacyclopent-3-ene

Independent distances (Å)		Amplitudes (Å)
r 1 (C – C)	1.322 ± 0.011	0.045 (fixed)
r 2 (C – C)	1.526 ± 0.007	0.053 ± 0.009
r 3 (C – H)	1.045 ± 0.013	0.090 (Fixed)
r 4 (Cl – Si)	2.068 ± 0.002	0.060 ± 0.003
r 5 (Si – C)	1.884 ± 0.003	0.060 (tied to U 4)
Dependent distances		
d 1 (Cl...Cl)	3.262 ± 0.007	0.101 ± 0.005
d 2 (Cl...C)	4.779 ± 0.022	0.242 ± 0.023
d 3 (Cl...C)	3.302 ± 0.011	0.101 (tied to U6)
d 4 (Cl...H)	5.111 ± 0.028	0.200 (fixed)
d 5 (Cl...H)	3.323 ± 0.009	0.150 (fixed)
d 6 (Cl...H)	4.065 ± 0.016	0.200 (fixed)
d 7 (Si...C)	2.604 ± 0.016	0.070 (fixed)
d 8 (Si...HO	3.624 ± 0.023	0.150 (fixed)
d 9 (Si...H)	2.536 ± 0.013	0.130 (fixed)
d10 (C...C)	2.889 ± 0.012	0.086 ± 0.018
d11 (C...C)	2.479 ± 0.014	0.086 (tied to U15)
d12 (C...H)	3.608 ± 0.017	0.271 (fixed)
d13 (C...H)	2.234 ± 0.015	0.130 (fixed)
d14 (C...H)	3.433 ± 0.023	0.271 (fixed)
d15 (C...H)	2.095 ± 0.013	0.130 (fixed)
d16 (C...H)	2.049 ± 0.020	0.130 (fixed)
d17 (H...H)	4.457 ± 0.028	0.200 (fixed)
d18 (H...H)	4.128 ± 0.021	0.200 (fixed)
d19 (H...H)	4.015 ± 0.028	0.200 (fixed)
d20 (H...H)	2.533 ± 0.018	0.120 (fixed)
d21 (H...H)	2.353 ± 0.024	0.150 (fixed)
d22 (H...H)	1.682 ± 0.022	0.110 (fixed)

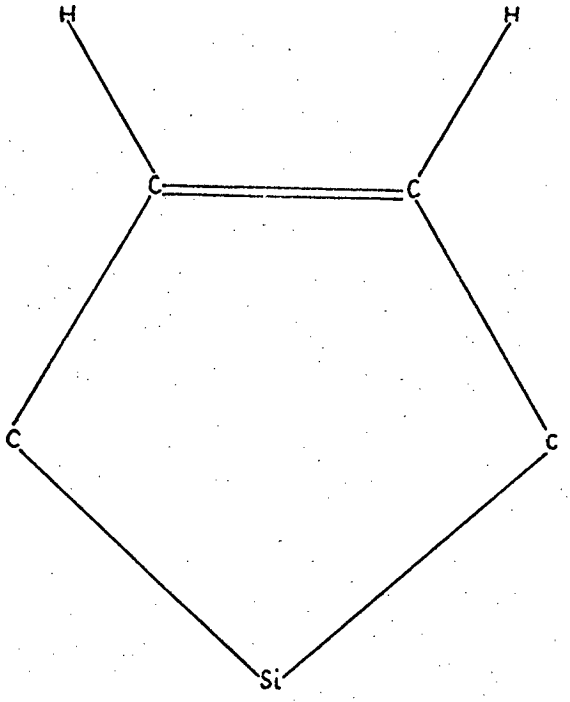
Table IV (continued)

Independent angles

1 (C – C – C)	120.90 ± 0.28
2 (Cl – C – Cl)	104.12 (fixed)
3 (H – Si – H)	107½36 (fixed)
4 (tilt)	0.00 (fixed)

Dependent angles

1 (C – Si – C)	99.04
2 (Si – C – C)	100.12



1° : 1 Å

Fig V

References

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Appendix II

The N.M.R. spectra of some organic π derivatives of silane and germane

Vinyl Germane

The spectrum of vinyl germane was recorded inssolution in "Actron" with the instrument locked on T.M.S. The spectrum consisted of two sets of signals, a doublet at about 6.2 τ and a complex set of lines centred at about 4.0 τ. This was found to be a second order ABC system on simple trial analysis, characteristics of vinyl compounds. The resonance at high field was due to the germyl protons split by the vinylic hydrogen. A quartet at the low-field side of the complex region was found to collapse to a single line on decoupling the germyl protons and the spectrum simplified down to twelve lines. Similar decoupling of the quartet collapsed the germyl proton doublet.

Analysis of the decoupled vinyl spectrum was carried out using a computer simulated spectrum. The programme used was a version of the programme LAOCOON 3 written by A. A. Bothner-By and S. Castellano[1]. The programme operated in two modes. A first non-iterative mode, given initial estimates of the chemical shifts and coupling constants, produced a set of theoretical frequencies and intensitites. Line numbers were then matched with the observed frequencies. In the iterative calculation a set of parameters was obtained that minimised the sum of the weighted squares of the deviations between observed and calculated frequencies. The results were then plotted on a graph. The spectrum with observed frequencies and calculated frequencies toghether with intensities are shown in Figure I and table I.

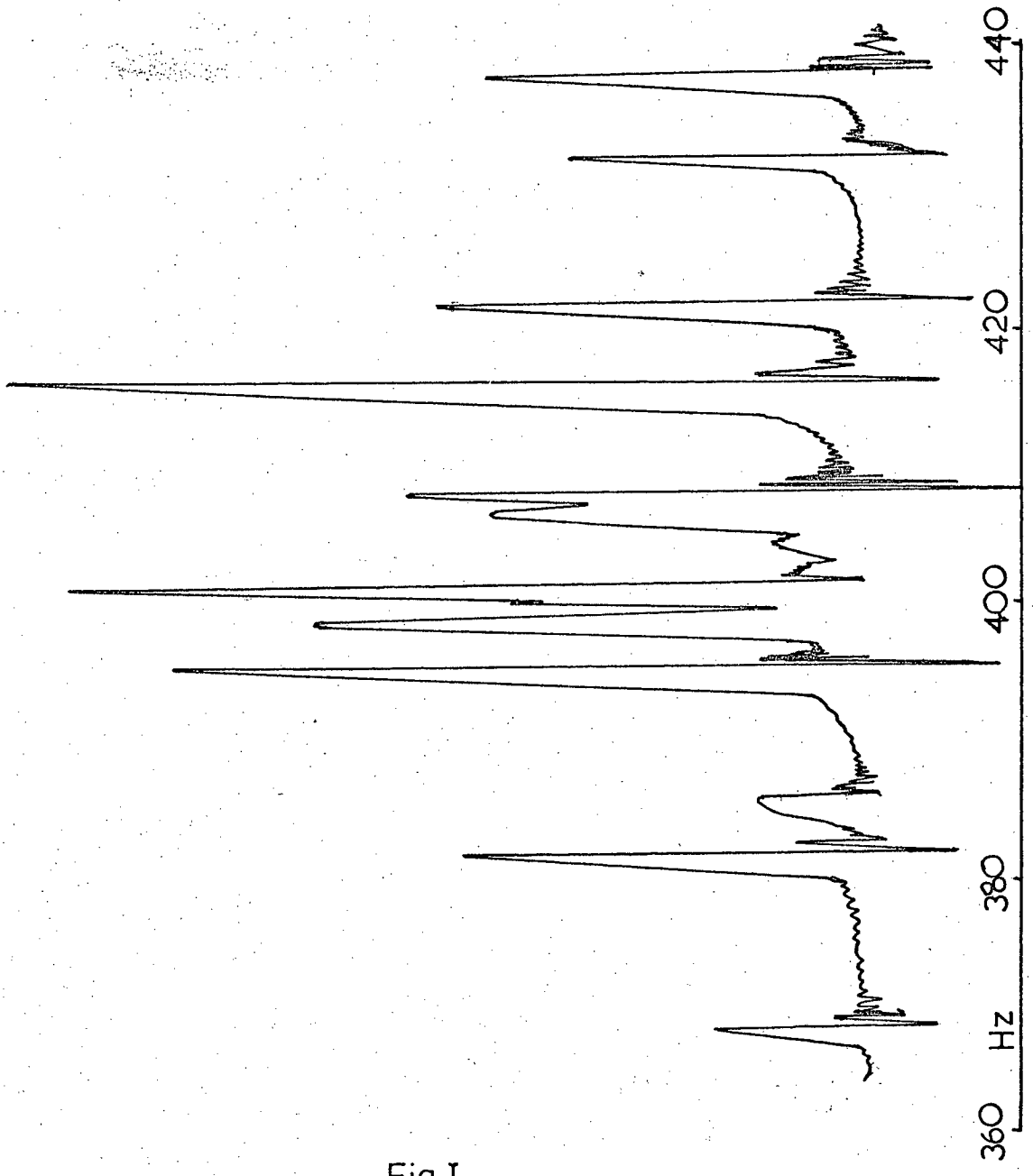


Fig I

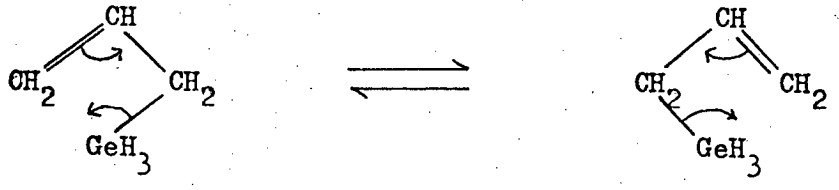
Decoupled ^{1}H N.M.R. Spectrum of Vinyl Germane, (vinyl region).

A good agreement was found for the transition frequencies but not for the intensities. Changing the assigned line numbers of the observed frequencies or reversing the sign of the coupling constants did not produce any better a fit. Thus, the decoupling may affect the intensity distribution in some way. The 'best-fit' parameters are given in table II. According to Reilly and Schwalen[2] the sum of the coupling constants is proportional to the electronegativity of the vinyl substituent. The value of 35.06 c/s is consistent with values of 32 c/s and 38.5 c/s for carbon and silicon respectively[3] and similar to that found for hexavinyldigermane, $J = 36.3$ c/s[4].

Considering the relative chemical shifts of vinyl germane, these show a shift to lower field from propene, (10). A similar shift in hexavinyldigermane has been interpreted in terms of less shielding from reduced electron density, caused by $(\pi \rightarrow d)\pi$ back-bonding to the Ge 4d levels, with which this agrees[4]. However, according to Ebsworth[5] interpretation of chemical shifts in terms of $(\pi \rightarrow d)\pi$ bonding is not on a sound basis.

Allyl Germane

The N.M.R. spectrum of allyl germane was taken in solution in arcton, the instrument being locked on T.M.S. Spectra were recorded at variable temperature down to -70° C but no change was observed, thus indicating that the molecule may not be subject to any fluxional behaviour at or below room temperature, i.e.:



If this does occur then the coupling between protons would be lost as bonds were broken and made. The rate of fluxing in this temperature range may be too fast or too slow to be detected in the N.M.R. time scale.

The spectrum was found to be first order and the measured coupling constants and chemical shifts are shown in table III. The signals in the vinyl region were assigned to protons C, A and B in order of shift to higher field. Coupling of protons A, B or C with each other and with D would be expected to produce a doublet of doublets of triplets. This was only found resolved for proton C, the triplets overlapping in A and B. E occurred at higher field, in the germyl resonance region and was split into a triplet by D. Proton D was split by all other protons and occurred at high field as a doublet of quartets of triplets, the triplets again being overlapping doublets because of the similarity of J_{AD} and J_{CD}.

Vinyl Silane

The spectrum was run in CCl_4/T.M.S. and consisted of a complex band at 4.0 τ and a doublet at 6.2 τ, the SiH_3 region. Decoupling of the silyl protons gave a simple 8 line spectrum in the vinyl region. This could be analysed as a first-order spectrum, assuming the gem coupling constant to be zero. This is consitent with a study of vinylic systems in which it was found that as the $\hat{HCH}$ gem angle increased, J gem became negative, being zero at 125° [6]. The angle predicted for vinyl silane from a microwave structure determination is 120° [7]. Lower electron density in the π bond might be expected to cause $\hat{HCH}$ to increase by diminished electron-pair repulsions. However, vinyltrimethylsilane gives an unperturbed ABC spectrum[8] whilst vinyltrichlorosilane gives a singlet

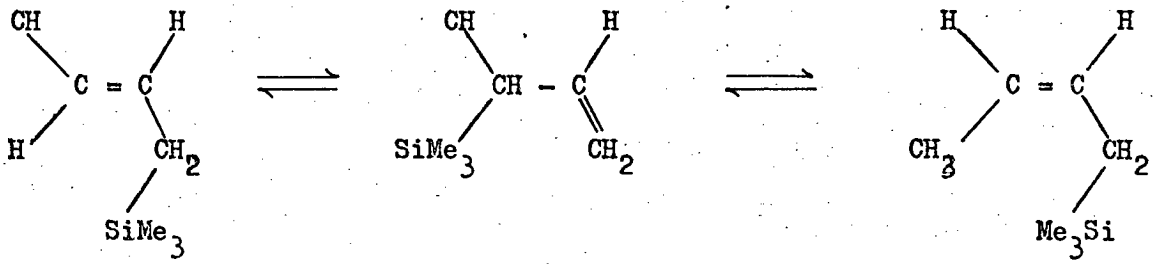
at 3.8 τ with ^{29}Si side bands[8] i.e. all the vinylic protons would appear to be equivalent, possibly due to very large deshielding by the chlorine atoms. Vinyl silane could be an intermediate state of affairs producing a highly perturbed A.B.C. spectrum.

Analysis of the spectrum on a first order basis was aided by considering together lines from decoupling experiments. The molecular parameters are given in table IV.

As in other vinylsilanes, $ViMe_3Si$ and Vi_2Me_2Si[9] and $Vi_nPh_{(4-n)}Si$, the downfield shift from propene can be interpreted in terms of $(\pi \rightarrow d)\pi$ bonding.

Allyl Silane

The spectrum was run in pure T.M.S. at room temperature, arcton at low temperature and toluene at high temperature. The spectrum was of interest as there is again the possibility of fluxional behaviour. A silyl migration, similar to this possible fluxional behaviour has been found to occur in 4 trimethylsilylbut-2-ene[10];



This has been rationalised in terms of a sigmatropic 1:3 shift involving an anti-symmetric Si 3p orbital.

The spectrum was found to be identical with that of allyl germane and the parameters are listed in table III. However the vinyl region was more complex and not all the parameters were found. The parameters agree well with those found for but-1-ene[11].

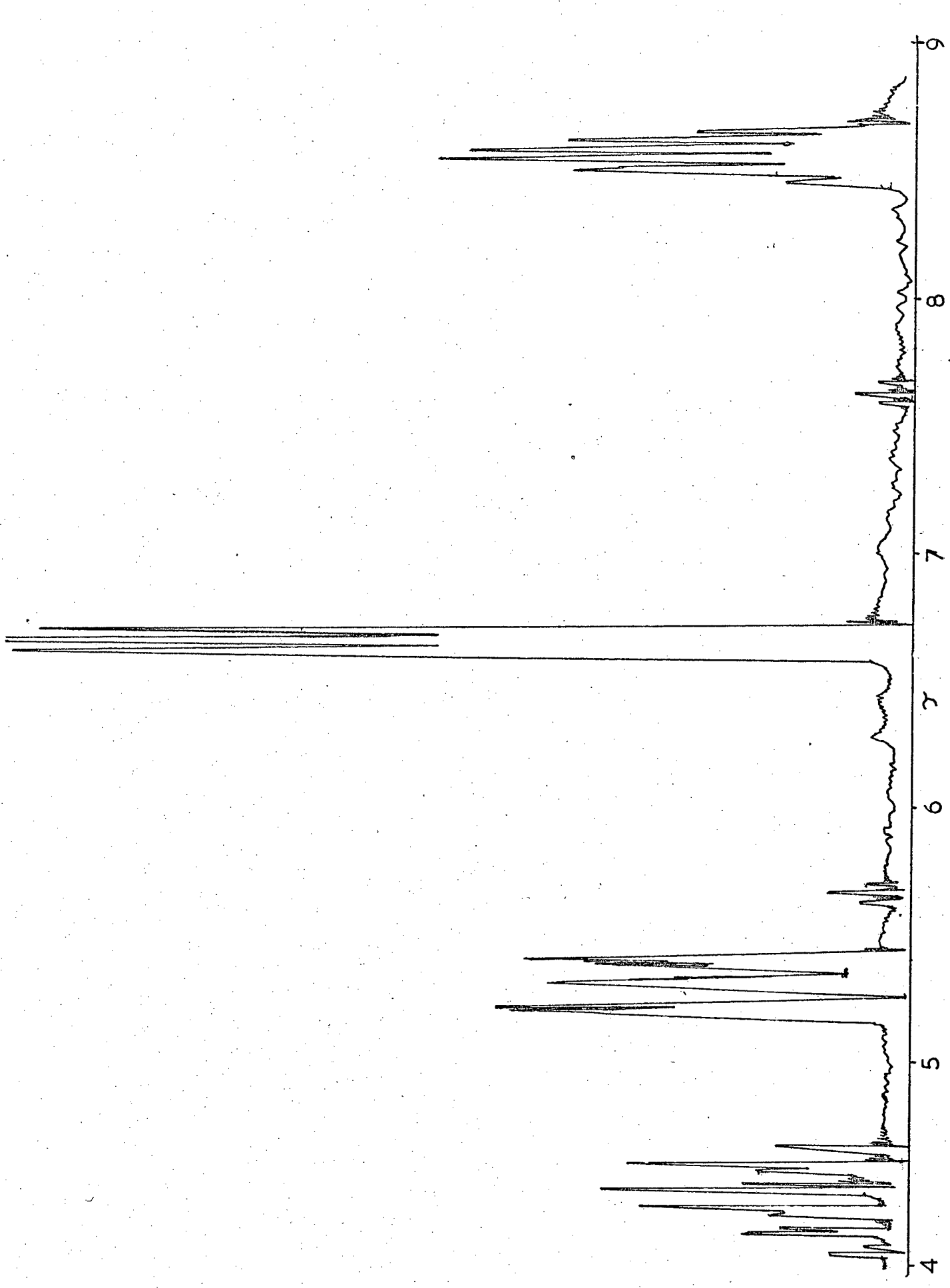


Fig II

^1H N.M.R. Spectrum of Allyl Silane

TABLE I

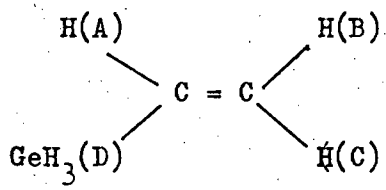
N.M.R. Transitions of Vinyl Germane

Shifts are in c/s from T.M.S. ($\pm$ 0.2 in observed frequency)

observed frequency	calculated frequency	observed intensity	calculated intensity
-631.7	-631.4	0.35	0.263
-619.0	-619.1	0.83	0.796
-615.0	-614.7	0.24	0.186
-605.8	-606-2	1.61	0.963
-602.3	-602.4	1.46	2.483
-599.9	-600.1	2.50	2.584
-594.1	-593.9	0.72	0.675
-592.9	-593.3	0.92	0.306
-585.0	-584.9	1.95	1.774
-579.0	-578.8	0.91	0.860
-568.2	-568.1	0.54	0.550
-562.2	-562.1	0.89	0.475

TABLE II

M.M.R. Parameters for Vinyl Germane. ($\pm$ 0.001 c/s or p.p.m.)



J_{AB} = 12.516 c/s

J_{AC} = 19.612 c/s

J_{BC} = 2.934 c/s

J_{DA} = 2.4 c/s ($\pm$ 0.1 c/s)

τ_A = 3.883

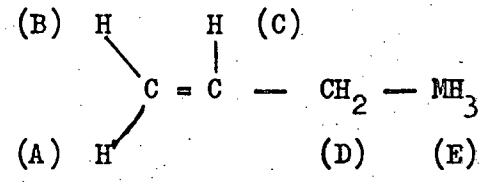
τ_B = 4.005

τ_C = 4.238

τ_D = 6.149

TABLE III

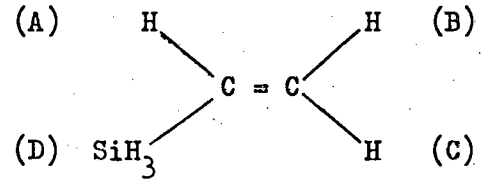
N.M.R. Parameters of allyl silane and germane ($\pm$ 0.1 c/s)



M =	Si	Ge	C	M =	Si	Ge
J_{AB}	-	1.8	1.75	τ_A	-	5.09
J_{AC}	16.9	16.8	16.18	τ_B	-	5.21
J_{AD}	1.4	1.3	1.33	τ_C	4.33	4.07
J_{BC}	9.4	9.8	10.02	τ_D	8.46	8.14
J_{BD}	0.8	0.9	-	τ_E	6.77	6.43
J_{CD}	7.2	7.9	6.40			
J_{DE}	3.8	3.2	2.08			

TABLE IV

N.M.R. Parameters of Vinyl silane. ($\pm$ 0.1 c/s)



J_{AB} = 11.3 $\quad\quad$ τ_A = 3.99

J_{AC} = 15.0 $\quad\quad$ τ_B = 4.09

J_{BC} = 0.0 $\quad\quad$ τ_C = 4.11

J_{AD} = 0.6 $\quad\quad$ τ_D = 6.17

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Appendix III

Some reactions to Fluorosilanes

Introduction

Little has been reported in the literature of the chemistry of fluorosilanes, possibly because of the difficulty in preparing simple species. Trifluorosilane was first prepared in 1944[10] and has since been well characterised. Bromo and chlorofluoro silanes have been prepared by heating mixtures of SiF_4 with $SiBr_4$, or $SiCl_4$, for several days at 150° C. in the presence of aluminium chloride as a catalyst[1]. Recently a preparation of SiF_3Br and SiF_3Cl has been developed involving cleavage of the Si - O bond in methyoxytrifluorosilane with the corresponding boron trihalide, the methoxy compound being obtained by halogen exchange of the corresponding chlorine compound with antimony trifluoride using an antimony pentachloride catalyst[2].

$$MeOSiCl_3 + SbF_3 \longrightarrow MeOSiF_3 + SbF_xCl_{3-x}$$

$$MeOSiF_3 + BX_3 \longrightarrow MeOBX + SiF_3X$$

The cleavage reaction did not work with hydrogen bromide or iodide in either the liquid of gaseous phases. Fluoriodosilanes were first prepared by reaction of SiF_4 with SiI_4 at 700° C[3] and by reaction of SiF_4 or Na_2SiF_6 with aluminium iodide at 300° C[4]. Recently SiF_2 has been found to combine with iodine yielding SiF_3I and SiF_2I_2[5]. Trifluorosilyliodide was thought to be[6] very susceptible to disproportionation, however during the course of this work a paper appeared on the preparation and properties of SiF_3I and SiF_2I_2 by Aylett etal[7]. They were prepared by cleavage of the Si - N bonds in dialkylaminofluorosilanes by hydrogen

iodide in 70 - 80% yield. This is analagous to the preparation of silyl iodide from trisilylamine by cleavage with HI.

$$SiF_{(4-x)}(NMe_2)_x + 2xHI \longrightarrow SiF_{(4-x)}I_x + xNH_2Me_2I$$

Excess HI with the trifluoroamine gave triiodofluorosilane showing that it is not only produced by disproportionation of the mono-iodide. The disproportionation of SiF_3I was found to proceed by only 10% in the liquid phase after two weeks, the compound being thermally stable up to its boiling point, ($-37^{6}C$).

The trifluorosilylpseudohalides have also been prepared by reaction of SiF_3Br with the silver salt, AgNCY, (Y = O, S, Se), similar reactions occurring with mercury salts[7]. These reactions are analagous to the exchange reactions of silver salts with silyl halides[8]. The isothio and isoselenocyanate were found to decompose rapidly at room temperature, n.m.r. studies indicating disproportionation into SiF_4 and SiF_2 derivatives of selenium, this being similar to the behaviour of the silyl compounds. The isocyanate was found to be slow in disproportionating but underwent reaction with HBr, cleavage of the Si - N bond occurring. Other silver salt reactions have lead to the preparation of some trifluorosilylesters of perfluorocarboxylic acids[9];

$$SiF_3Br + AgO_2CR_F \longrightarrow R_FCO_2SiF_3 + AgBr$$

$$(R = CF_3,\ C_2F_5,\ C_3F_7)$$

Again the compounds were found to be unstable, especially in the liquid phase above $-30^{\circ}C$. Generally, trifluorosilyl derivatives are susceptible to base-catalysed disproportionation, as are silyl derivatives to a lesser extent. Attempted preparations of the alkyl carboxylic acids produced only SiF_4, due to decomposition catalysed by the basic oxygen of the carboxyl group.

The disproportionation produces SiF_4 and so makes handling of SiF_3 compounds difficult. Traces of water tend to produce hexafluoro-disiloxane which is again difficult to separate.

Many of the reactions attempted with SiF_3Cl and SiF_3Br gave only the starting materials. The compounds were found to be very stable, unlike others mentioned. This could be connected with the relative strength of the Si - X bonds. The P.E. spectra indicate the I.P. of the Si - Cl to be less than that of the C - Cl bond showing the electrons to be tightly held.

Attempted preparations

Trifluorosilyliodide

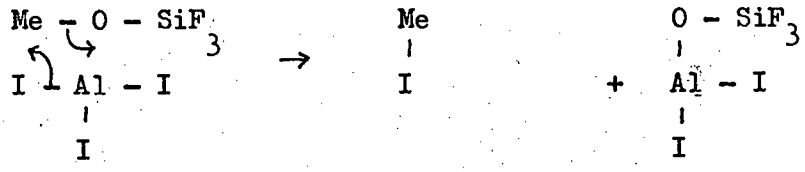
The preparation of SiF_3I was initially attempted by a number of routes, to obtain a sample for P.E.S. Iodine readily cleaves Si - H bonds at -30° C, giving Si - I bonds[11] and stannic chloride readily cleaves Si - H bonds[12]. Thus reactions between I_2 or stannic iodide and SiF_3H were attempted but no reaction occurred. The reaction vessel was irradiated with a U.V. lamp and heated to 180° C with SnI_4, (Mpt.).

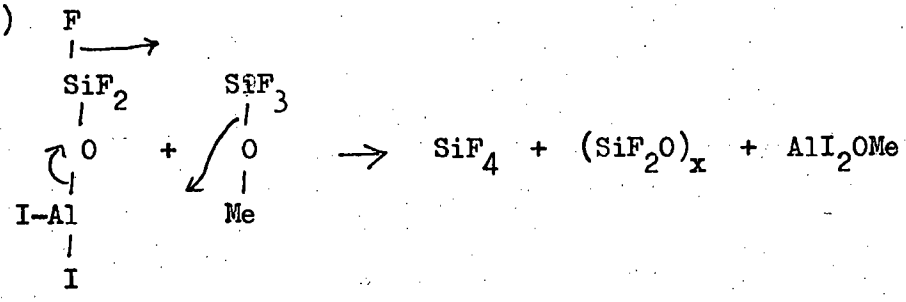
The attempted preparation of SiF_3I by cleavage of the Si - O bond in SiF_3OMe with BI_3, SnI_4 or I_2 was unsuccessful. Aluminium iodide, used for iodinating silanes[13] reacted at -78° C to give 1 mole of methyl iodide, 1 mole of SiF_4 and a white solid from 2 moles of SiF_3OMe. This represents either an acid catalysed disproportionation of SiF_3I or more likely a cleavage of both the Si - O and C - O bonds, methyl alcohol being cleaved by alumimium iodide to give methyl iodide.

The stoichiometric reaction is:

$$2SiF_3OMe + AlI_3 \longrightarrow SiF_4 + MeI + F_2SiO_2MeAlI_2$$

but the solid is probably an F - Si - O polymer;

(1) 

(2) 

Reaction by Aylett et al of AlI_3 with SiF_4 at 200° C gave only SiI_4.

Tris (trifluorosilyl) amine

The reaction between ammonia and trifluorosilylchloride was carried out in a manner identical to that for trisilylamine[21]. Irrespective of which reactant was in excess, the combining ratio varied between 1:2:5 and 1:3.0 of SiF_3Cl : NH_3. Ammonia was always added to the SiF_3Cl to reduce the possibility of any base-catalysed disproportionation. Reaction was immediate with the formation of a white solid and the evolution of much heat. Fractionation of the products gave either unreacted SiF_3Cl or ammonia and a trace, (0.05 m. moles) of substance condensing at 153°K. The I.R. spectrum and plausible assignments are given in table I indicating the product to be $(SiF_3)_2NH$ or SiF_3NH_2. However the N - H or NH_2 deformation is low and since it is usually weak in aliphatic secondary amines, the primary amine would seem the more probable. However there is only one apparent N - H stretch. This spectrum is very similar to that given by the product of the reaction between SiF_3I and excess ammonia, again involatile at 153°K and thought to be consistent with SiF_3NH_2.

The reaction;

$$SiF_3Cl + 2NH_3 \longrightarrow NH_2SiF_3 + NH_4Cl$$

is analagous to that reported by Aylett between SiF_3I and dimethyl-amine to give N-N-dimethyltrifluorosilylamine.

Thus $(SiF_3)_3N$ cannot be isolated by preparation from SiF_3Cl and ammonia, possibly being unstable under these reaction conditions. Its formation is not hindered sterically as $(SiCl_3)_2NSiF_3$ has been prepared[14].

Trifluorosilylcyanide

Attempts to prepare trifluorosilylcyanide by streaming trifluorosilylchloride or bromide through freshly prepared and dried silver cyanide produced only a trace of HCN, unlike the analogous reaction reported by Aylett between mercuric cyanide and trifluorosilyliodide giving SiF_3CN. An exchange reaction between silyl and germyl cyanide and SiF_3Br gave only a trace of GeH_3Br and a white solid but no bands in the i.r. spectrum attributable to SiF_3CN.

An exchange between Me_3SiCN and SiF_3Br in solution in benzene was attempted, the reaction being following in an n.m.r. tube. After 10 minutes, at R.T. the products were found to be Me_3SiBr, Me_3SiF and Me_3SiCN in a ration of 1:3:3 from a 1:1 mixture[15]. On standing for a few hours, the solution turned dark red and a solid was deposited. To check for reaction of SiF_3Br with the solvent, the reaction was carried out in arcton using a ^{19}F probe, but only SiF_3Br could be detected. A gas phase reaction of a 1:1 mixture produced a white solid, after a week, that slowly turned yellow. From 1 m. mole of each reactant, 0.25 m. moles of SiF_4 and 0.8 m. moles of a mixture of Me_3SiF and Me_3SiBr and HCN were

isolated. There were peaks at 410 cm^{-1} amd 10 35 cm^{-1} possibly due to SiF_3CN but no bands were found in the C ≡ N stretching region around 2000 cm^{-1}. No starting materials were recovered. SiF_4 could indicate a base catalysed decomposition of SiF_3Br, any bromine produced reacting with the Me_3SiCN to give $SiMe_3Br$ and HCN. SiF_3CN is reparted to polymerise in the gas phase to give a triazine[6] the appearance of the solid being indicative of such a reaction. Thus, although exchange may take place, the reaction is complex.

Hexafluorodisilane

As difficulty was found in the halogen exchange of Si_2Cl_6 with antimony trifluoride, other preparations were attempted. Reactions of the type;

$$2SiF_3Br + M \longrightarrow Si_2F_6 + MBr_2$$

(M = Na, Hg, Na/Hg)

gave only trace amounts of Si_2F_6 and the starting materials. This again shows the stability of the SiBr bond with respect to the lattice energy of the possible solid products, MBr or MBr_2.

Hexafluorodisiloxane

The chemistry of fluorosiloxanes has been quite well investigated. The structure of hexafluorodisiloxane has been determined[16] by the electron-diffraction method and found to have a skeletal angle of 157° indicating greater (p → d)π back-bonding to the Si3d orbitals than in disiloxane where the angle is 144°. Its i.r. and ^{19}F n.m.r. spectra[17] have recently been reported. Other fluorosiloxanes have also been reported. Hydrolysis[18] of SiF_4 has yielded $(SiF_3O)_2SiF_2$ as well as $(SiF_3)_2O$.

This has also been postulated[19] from mass spectral studies of the reaction of SiF_2 with SOF_2 which also produces $Si_2F_5OSiF_3$, linear $Si_3F_7OSiF_3$ and cyclic $(SiF_2O)_n$. $(SiF_2O)_x$ polymer has been produced by reaction of SiF_2 with oxygen and found to decompose to the more stable cyclic $(SiF_2O)_n$ on heating[19].

The preparation of hexafluorodisiloxane was initially attempted by simple halogen exchange of hexachlorodisiloxane with antimony trifluoride using an antimony pentachloride catalyst at elevated temperature. Use of both gas-solid and liquid-solid mixtures produces samples with an i.r. band around 600 cm^{-1}, indicating an Si - Cl stretching vibration. A mass spectrum indicated the presence of both $(SiF_3)_2O^+$ parent ions.

When SiF_3Br was passed over slightly moistened or dry mercuric oxide, SiF_4 and a trace of $(SiF_3)_2O$ were the only products. Aylett found an analogous reaction using SiF_3I, giving only $(SiF_3)_2O$ on dilution of SiF_3I with nitrogen.

The hydrolysis of SiF_3Cl was complete yeilding SiF_4 and HCl and a white solid. The reaction vessel, made of pyrex glass, was found to be slightly etched. Thus there appears to be a base-catalysed decomposition similar to that for SiF_3I.

$$2\ SiF_3Cl + H_2O \xrightarrow{r.t.} (SiF_3)_2O + 2HCl$$

$$(SiF_3)_2O \rightarrow {}^{1}/_{x}\ (SiF_2O)_x + SiF_4$$

With moist silver oxide SiF_3Br gave a viscous liquid with a vapour pressure of 14 mm, (v.p. of water = 10 m.m). A mass spectrum showed peaks with ${}^{m}/_{e}$ of 102 and 101 attributable to SiF_3OH^+ and also of much water. If SiF_3OH does form it might be expected to be more stable than the supposed SiH_3OH due to the electron withdrawing fluorine making the Si - O bond more polar[22].

An exchange reaction between his (tri-n-butyl tin) oxide and SiF_3Cl was attempted but only a trace $(SiF_3)_2O$ was found after a couple of days.

Hexafluorodisilylsulphide

The only reported fluorosilicon-sulphur compounds are SiF_2HSH and SiF_2HSiF_2SH[20] made by reaction of SiF_2 with H_2S. These mercaptans are more stable than the silylmercaptans due to the strengthening of the Si - S bonds by the fluorine. Disilysulphide is know to undergo an exchange reaction with germyl chloride to give digermyl sulphide. The exchange between disilylsulphide or digermylsulphide and SiF_3Cl was attempted but in both bases only the starting materials were recovered.

Distillation of the products of a gas-solid reaction between mercuric sulphide and SiF_3Br yielded SiF_4 and a trace of $(SiF_3)_2O$. The grease joints smelled strongly of hydrogen sulphide i.e. if any $(SiF_3)_2S$ was formed it may have been very susceptible to hydrolysis. Aylett found that the analogous reaction with SiF_3I gave $(SiF_3)_2S$ in the gas phase while a liquid-solid reaction gave the cyclic tetrafluorocyclodisilathiane $(SiF_2S)_2$. This is formed by decomposition of $(SiF_3)_2S$ in a similar way to that of $(SiH_3)_2S$ giving oligomer chains.

Conclusions

SiF_3Cl and SiF_3Br appear to be very stable to a number of reagents: elements, Lewis acids and weak bases although they do react with stronger bases, e.g. NH_3, in base-catalysed disproportionation reactions analogous those of the corresponding hydrides . This great stability is reflected in the ionisation potentials of the Si - X bonds, which are comparatively very high.

TABLE I

I.R. Spectrum of SiF_3NH_2 ($\pm$ 5 cm^{-1}) and assignments

3405	(w)	ν NH_2
1260	(w)	δ NH_2
1234	(s)	δ NH_2
1025	(s)	ν SiF_3
1008	(s)	ν SiF_3
977	(sh)	ν SiN
822	(m)	υ SiF_3
465	(w)	δ SiN
405	(m)	δ SiF_3

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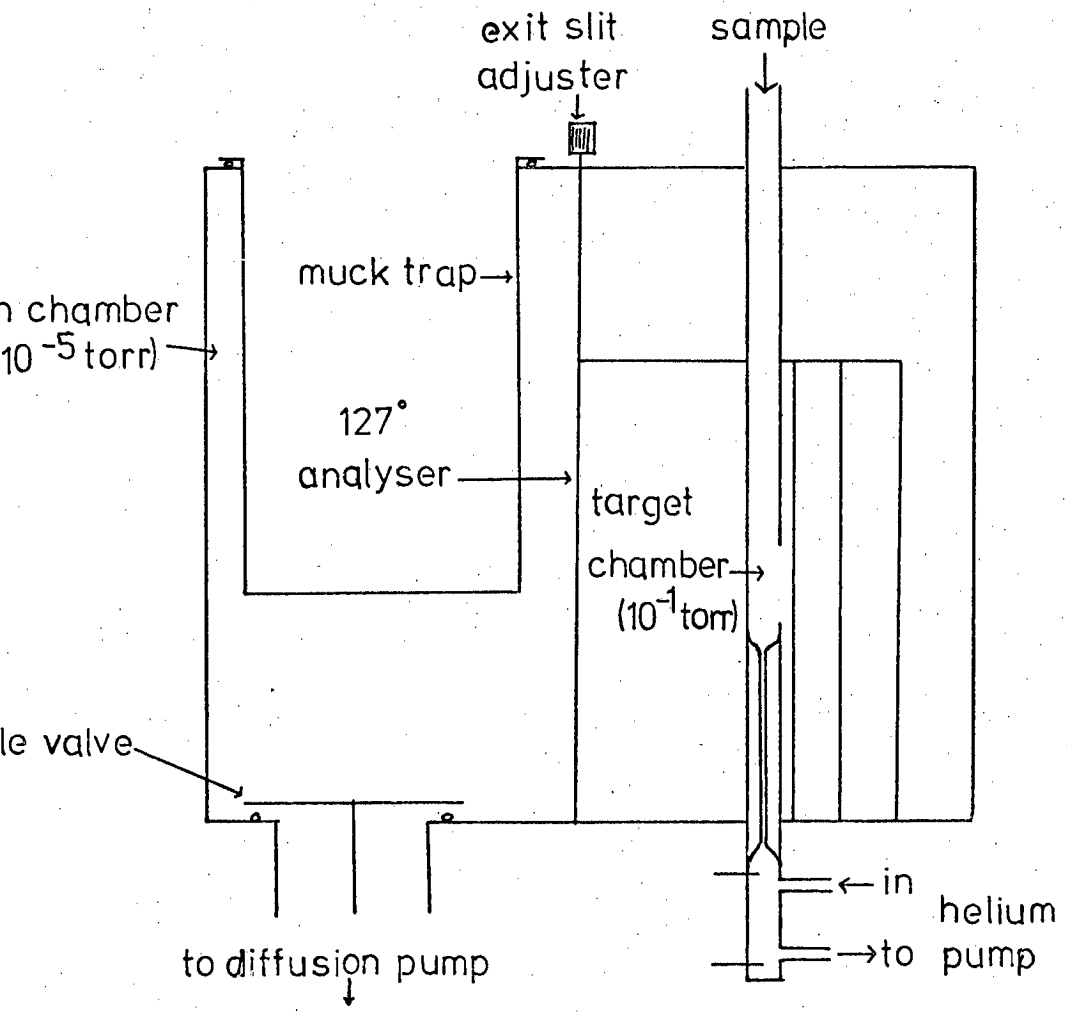

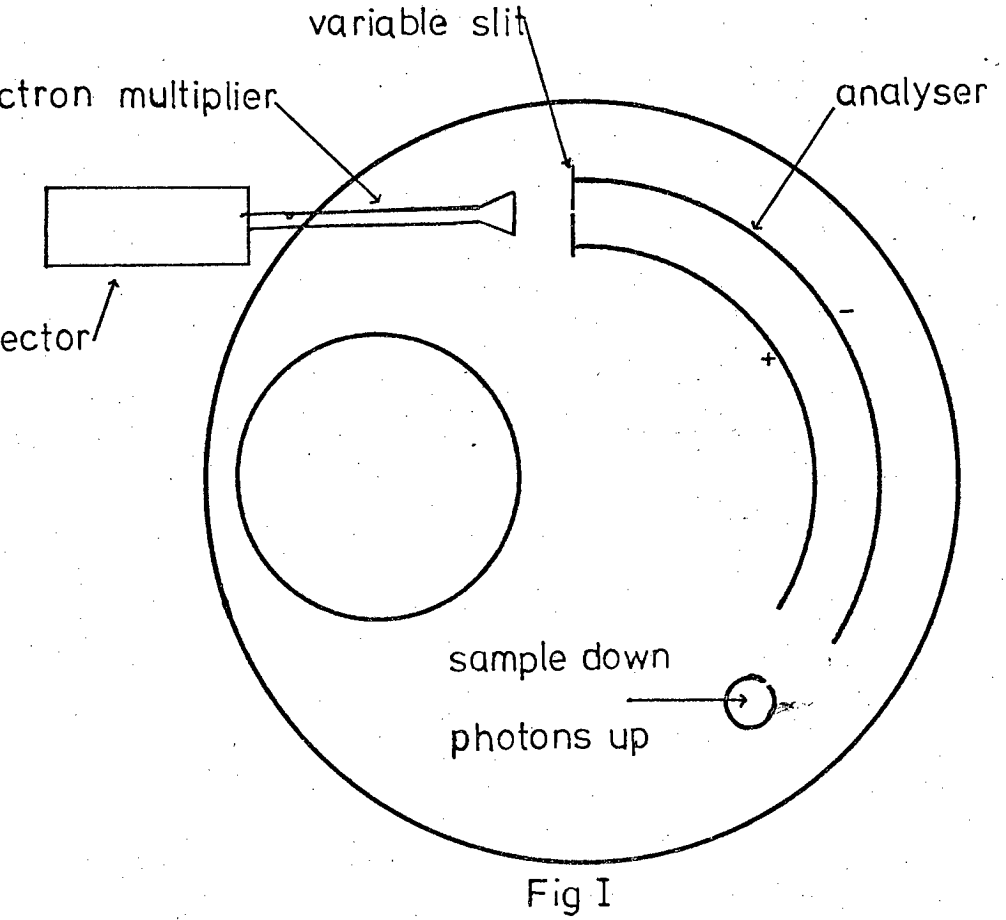

Fig I

Schematic representation of Perkin-Elmer PS 16
Photoelectron Spectometer

Appendix IV

Experimental Techniques and the preparation of starting materials and samples

The P.E. Spectrometer

The Spectrometer used was a commercially available Perkin-Elmer P.S. 16 instrument, first produced three years ago based on a design by D. W. Turner. The instrument employed a water cooled helium discharge lamp giving a photon source with a line energy of 584 Å, (21.22 eV), this being the strongest line in the emission spectrum and accounting for 98% of the emission in this spectral region. The single line avoids the necessity of a monochromator. The lamp was connected to the target chamber, where photo-ionisation occurred, by a fine capillary tube which allowed radiation to pass but prevented diffusion of the He. The helium was continuously pumped out from the lamp. After photo-ionisation, the ejected electrons passed initially through a 1 m.m slit and thence to the analyser. The electrostatic analyser consisted of two concentric plates of 127° section, the voltage between which was varied to deflect electrons of different kinetic energies between 0 and 15 eV. Earlier machines employed an electro-static retarding analyser but these gave bad signal-to-noise ratios[30]. The exit from the analyser was controlled by a variable slit, maximum opening 1 m.m, which was kept at a minimum for maximum resolution while maintaining a strong signal. The electrons then passed to an electron-multiplier and counting system. The main chamber which contains the analyser, target chamber, and electron-multiplier was maintained at a pressure of about 5×10^{-5} torr by continuous pumping with an oil diffusion pump backed by a rotary oil pump.

A baffle valve between the chamber anddiffusion pump allows the chamber to be let up to atmospheric pressure whilst maintaining the vacuum system under maximum vacuum. This was necessary for periodic removal and cleansing of the liquid nitrogen 'muck-trap' on which sample gases were condensed. Samples were bled into the instrument through a 'Hoke' needle valve connected to a stainless-steel inlet manifold. The optimum sample pressure was found by optimising the signal of the strongest peak of the spectrum. The sample gas flowed down a tube concentric with the light source, the target chamber being above the lamp. The samples, most of which were explosive, moisture sensitive and corrosive were introduced into the stainless steel manifold from a standard vacuum line containing 'Rotaflo' greaseless taps to avoid the presence of grease which dissolved many of the samples. However, frequent cleaning and pumping of the manifold valves and line were necessary. For certain very moisture sensitive samples e.g. SiH_2Cl_2, the system was dried by flushing with silyl chloride until the signal from HCl wasreduced to zero. Samples could be removed from the 'Muck-trap' by use of a large pot, the top of which was ground to take the rubber O-ring seal of the trap, the whole being connected to a vacuum line and the sample pumped off as the trap warmed up.

The spectra were recorded with a variable count rate up to a maximum of 5000 c.p.s. and a slow chart speed for maximum resolution. The calibration of the spectra, which was always carried out with the sample still in the instrument because of the effects of charge build up, was made using the doublet peaks of argon at 15.75 and 15.93 eV, kept in the instrument reservoir.

The Ar peaks were also used to frequently check the resolution of the instrument, a good resolution being 20 m.e.V. peak-width at half peak height for the $^2P_{\frac{3}{2}}$ peak at 15.75 eV. All peaks were expanded two-fold or five-fold and weak bands run at higher count rate in order to measure a more accurate vertical ionisation potential. Argon calibrations were put on all expanded bands because of a slight voltage shift in the recorder on using the expansion scale. Where recording fine structure, or when using a very low count-rate, (e.g. 150 cps.), the counting was integrated over 5 or 15 seconds and a very slow chart speed used to give a better signal-to-noise ratio and to increase resolution. Recently the spectrometer was fitted with a more powerful air-cooled lamp for photo-ionising the vapours of solids at high temperature. Hence some of the spectra are much better resolved. Previous to this adaptation, the instrument incorporated a heated charcoal column for purifying the helium of hydrogen, the purity of the discharge being checked by observing the discharge, displayed by a fibre optic, with a simple visible region spectrometer. A diagramatic representation of the apparatus is shown in Fig. I.

The He II spectra were recorded on a modified P.S. 16 instrument. The modification involved a lamp running at lower pressure but using a higher discharge current. The He I 584 Å line was still dominant and very small count rates (2 c.p.s.) and high integration times were required. The region above about 27 eV was obscured by the ionisation of helium itself. The spectra were calibrated from known peaks on the corresponding He I spectra.

Apparatus for preparations

All manipulations of volatile compounds were carried out in a Pyrex vacuum system of conventional design. High vacuum, necessary for the exclusion of air and moisture from the materials being handled, was maintained by means of a mercury diffusion pump backed by a rotary oil pump. Pressure inside the apparatus was measured using a spiral gauge with mirror, employed as a null point instrument with a lamp and scale.

The vacuum line was built up from detachable sections. This aided cleaning which was frequently necessary, to remove involatile solids deposited as decomposition products of the volatile species, notably the germyl and trifluorosilyl species. Apiezon L and N greases were used on the stop-cocks and ground glass joints. Most of the detachable reaction vessels were fitted with 'Rotaflo' teflon greaseless taps, care being taken not to place them near liquid nitrogen which rapidly caused leaks. The line was calibrated for volume using amolecular weight bulb. This enabled quantitative estimations of the amount of volatile materials present to be made rapidly from pressure readings.

In order to establish the purity of the samples used a number of methods were used. I.R. spectroscopy was used to identify samples and impurities, the latter being removed by trap-to-trap distillation in one of the two trap sections through traps surrounded by slush-baths of known temperature. For less well known samples, vapour-phase molecular weight determinations and vapour pressure determinations at various temperatures were made together with ^{1}H and ^{19}F n.m.r. spectra to determine any impurities. The constancy of vapour pressure was taken as a criterion

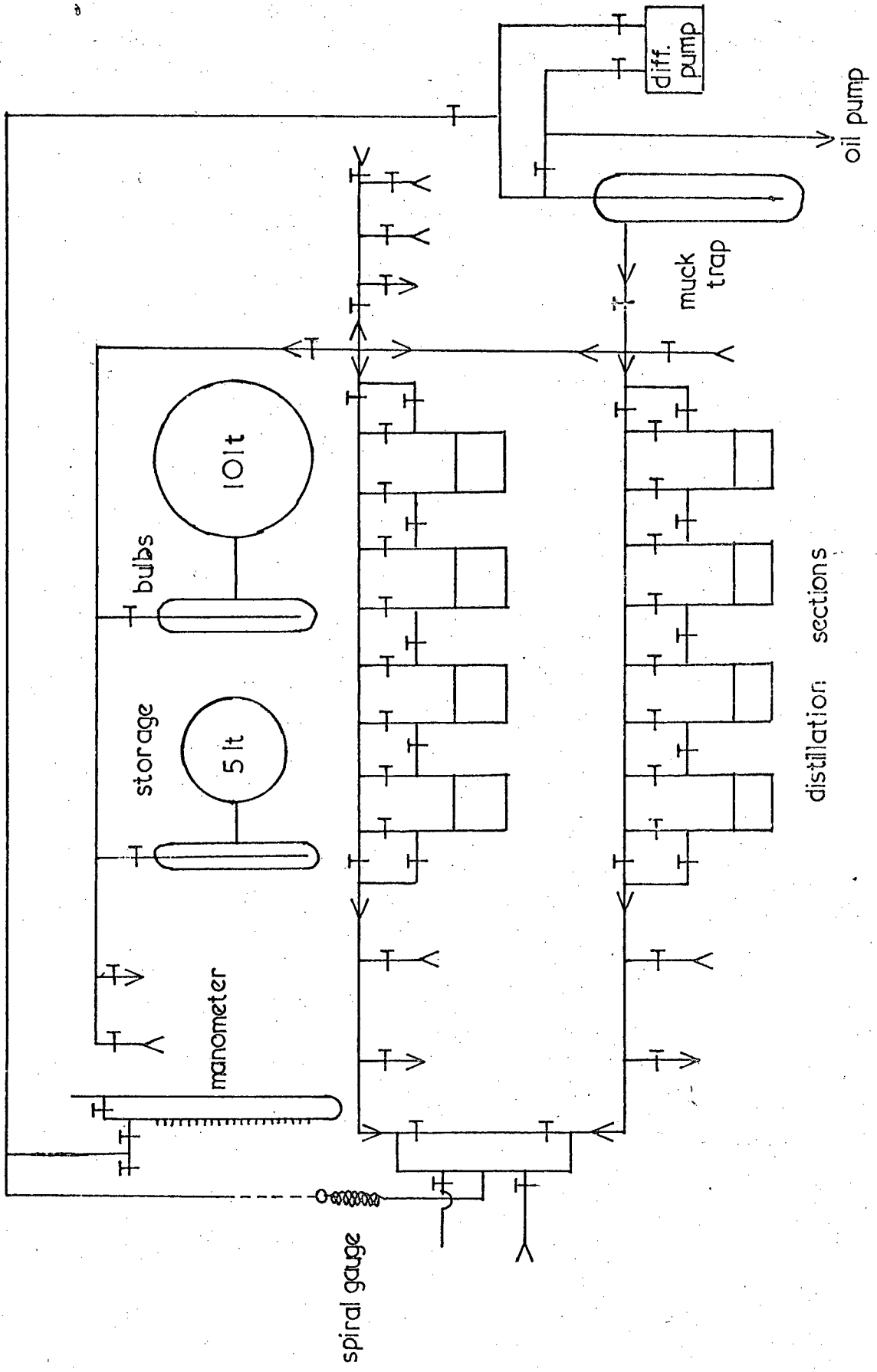

Fig II

Vacuum line for preparations

of purity.

Infra-red spectra were recorded using a Perkin-Elmer 457 grating spectrophotometer. The vapour cell was 10 cm in length and fitted with CsI or KBr plates using Apiezon W cement. The plates were periodically removed for polishing and cleaning. Samples were usually run at less than 5 mm pressure except when finding impurities. Less volatile samples were frozen in using cotton wool soaked in liquid nitrogen.

Proton nuclear magnetic resonance spectra were recorded using a Varian HA 100 spectrometer operating at 100 MHz. This was fitted with a variable temperature probe and an external frequency supply for decoupling experiments. Fluorine spectra were recorded on an XL 100 instrument using a fluorine probe. Samples, about 0.25 m moles, were sealed in conventional pyrex tubes with ground glass bottoms the solvent usually being T.M.S. or Arctan.

Mass spectra were recorded on an A.E.I. M.S.9 spectrometer with an ionising voltage of 70 eV, smaples being bled in at very low pressure from a two litre bulb. Ultra-violet spectra were recorded on a Unicam S.P. 800 spectrophotometer, using a deuterium lamp, the sample being placed at low pressure ($\sim$ 1 mm) in one of a pair of 100 mm. matched glass cells.

Preparation of samples and starting materials

Procedures used to prepare and/or purify the many compounds used in the course of this work are listed briefly below. The silyl and germyl starting materials were generally prepared by well documented techniques so no detailed account of these is given. Usually, samples for P.E. spectra were prepared in one or two milli-mole aliquots.

Silyl bromide was prepared by the method of Kumer and Fitz on a 200 m mole scale[1].

$$4PhSiCl_3 + 3LiAlH_4 \rightarrow 4PhSiH_3 + 3LiCl + 3AlCl_3$$

$$PhSiH_3 + HBr \xrightarrow{-78^\circ C} PhH + SiH_3Br$$

Purification and separation was achieved by distillation from -96° C into -120° C. The reduction was carefully carried out under nitrogen in di-n-amyl ether.

Silyl chloride was prepared by streaming silyl bromide through an excess of dried mercuric chloride[2], giving a conversion of about 95%. Separation was achieved by passage through -120°C and into -130° C.

$$2\,SiH_3Br + HgCl_2 \longrightarrow HgBr_2 + 2SiH_3Cl$$

Silyl fluoride was prepared by streaming silyl chloride through an excess of antimony trifluoride[3].

$$SiH_3Cl + SbF_3 \longrightarrow SiH_3F + SbF_{3-x}Cl_x$$

Silyl iodide was prepared by reaction between trisilylamine and hydrogen iodide in the gas phase, the hydrogen iodide being added to the amine.

$$(SiH_3)_3N + 4HI \longrightarrow 3SiH_3I + NH_4I$$

The iodide was condensed at -120° C.

Dichlorosilane was prepared by chlorination of silyl chloride with stannic chloride[4]. The yield was low (10%) and the reaction slow ($\sim$ 1 week).

$$SiH_3Cl + SnCl_4 \longrightarrow SiH_2Cl_2 + HCl + SnCl_2$$

The dichloride was condensed at -120° C, residual sily chloride being pumped through.

Difluorosilane was prepared by streaming dichlorosilane through antimony trifluoride[5].

$$SiH_2Cl_2 + SbF_3 \longrightarrow SiH_2F_2 + SbF_{3-x}Cl_x$$

Dibromosilane was prepared by streaming diiodosilane through a column packed with fresh silver bromide mixed with ground glass giving 100% conversion[5].

$$SiH_2I_2 + 2Ag\,Br \longrightarrow SiH_2Br_2 + 2AgI$$

Diiodosilane was prepared by reaction of HI with SiH_4[5].

Germyl bromide and dibromide were prepared by the bromination of germane with HBr using an aluminium bromide catalyst and excess germane[5].

$$GeH_4 + HBr \longrightarrow GeH_3Br + GeH_2Br_2 + GeHBr_3$$

The bromide was pumped off the dibromide at -78° C.

Germyl chloride and dichloride were prepared by streaming the corresponding bromides over mercuric chloride[5].

$$2GeH_3Br + HgCl_2 \longrightarrow 2GeH_3Cl + HgBr_2$$

Diiodo germane and germyl iodide were prepared by reaction between HI and an equimolar mixture of germyl chloride and dichlorogermane. The diiodide was unstable and a solid[5].

Difluoro germane was prepared by streaming dibromogermane through fresh lead fluoride giving 95% conversion.

$$GeH_2Br_2 + PbF_2 \longrightarrow GeH_2F_2 + PbBr_2$$

Germyl Fluoride was similarly prepared from germyl bromide and silver fluoride. As with the other germyl halides, the fluorides were very unstable at R.T. and difficulty was found in taking spectra.

Germane was prepared by the reduction of GeO_2 by Potassium borohydride in acid solution, (Acetic acid). CO_2 was removed with KOH solution and digermane was a side-product[5].

$$HGeO_3^- + BH_4^- + 2H^+ \longrightarrow GeH_4 + H_3BO_3$$

Hydrogen iodide was prepared by dehydration of a 50% aqueous solution with phosphorus pentoxide.

Disilylselenide and telluride were prepared by reaction between silyl bromide and potassium selenide[6] or lithium telluride[7] in dimethyl ether at 177° K,

$$2SiH_3Br + M_2Y \longrightarrow (SiH_3)_2Y + 2MBr$$

The salts were first prepared by dissolution of the respective elements in liquid ammonia at -64° C.

Disilylsulphide was prepared by the reaction between H_2S and trisilylamine[8].

$$(SiH_3)_3N + 2H_2S \longrightarrow (SiH_3)_2S + NH_4\,SSiH_3$$

Digermylsulphide, selenide and telluride were prepared by exchange between the corresponding silyl derivative and germyl bromide[6]

$$(SiH_3)_2Y + 2GeH_3Br \longrightarrow (GeH_3)_2Y + 2SiH_3Br$$

These samples were handled as little as possible, due to absorption in grease, especially by the tellurides.

Silyl and Germyl mercaptans were isolated from equilibrium mixtures with hydrogen sulphide and the corresponding sulphide.

$$(MH_3)_2S + H_2S \rightleftharpoons 2MH_3SH$$

The equilibria took about two months to establish but the thiols could not be obtained pure. They were distilled out of -96° C into -120° C. The preparations were carried out in greaseless tap ampoules with an excess of hydrogen sulphide to force the equilibrium to the right. The i.r. of silyl mercaptan agreed with the literature value[9] that of germyl mercaptan giving peaks at 2095, 2112, 850, 825, 817, 560 and 412 cm^{-1}.

Silyl selenol was separated from a mixture of disilylselenide and hydrogen selenide by condensing at -96° C. Hydrogen selenide was not

removed, to prevent the very rapid decomposition of the selenol.

Trisilylphosphine was prepared by reaction of silyl bromide on KPH_2 at -64° C in dimethylether[10].

$$3\ SiH_3Br + 3KPH_2 \longrightarrow P(SiH_3)_3 + 2PH_3 + 3KBr$$

The purity was checked with an i.r. spectrum[12].

Trisilylarsine was prepared by reaction between lithium arsenide and silyl bromide in dimethylether at 177° K. The lithium salt was formed by dissolution of the elements in liquid ammonia.

$$Li_3As + 3SiH_3Br \longrightarrow (SiH_3)_3As + 3LiBr$$

Trigermylphosphine was prepared by exchange between trisilylphosphine and germyl bromide[11].

Trislylamine was prepared by the gas phase reaction of ammonia with excess silyl chloride, to avoid base-catalysed decomposition[13].

$$SiH_3Cl + 4NH_3 \longrightarrow (SiH_3)_3N + 3NH_4Cl$$

Trigermylamine was prepared in a similar fashion, by reaction between excess germyl chloride and ammonia. The amine being particularly unstable was stabilised by dilution with argon[14] to avoid formation,

$$(GeH_3)_3N \longrightarrow (GeH_2)_n + NH_3$$

of polymer. The apparatus was connected directly to the P.E. machine vacuum line. Wide slits were necessary due to the dilution of the sample. The first band was not thought to be the He β line of GeH_3Cl as it did not diminish in intensity with respect to that of the bands due to germyl chloride, present to avoid the decomposition.

Disilane, methylsilane, vinyl silane, allyl silane and silacyclopent-3-ene were all prepared by reduction of the corresponding chloro-silanes, obtained commercially, with lithium aluminium hydride in di-n-amyl ether, under a reduced pressure of dry nitrogen.

Silyl germane was prepared by the method of Varma and Cox[15], by reaction of a solution of potassium silyl with germyl chloride at 0° C. The germyl chloride was added in small amounts to avoid the formation of disilane or digermane, volatiles being pumped off after each addition. The addition was aided by condensation of the GeH_3Cl into a side arm. The potassium silyl was prepared by reaction of silane with freshly ground KOH in monoglyme, the excess of which was filtered in a glass sinter incorporated in the glass sealed apparatus.

$$K^+SiH_3^- + GeH_3Cl \longrightarrow SiH_3GeH_3 + KCl$$

Silylarsine was prepared by reaction of lithium tetraarsino-aluminate, prepared by reaction of lithil with arsine, with silyl bromide in diglyme[16].

$$LiAlH_4 + 4AsH_3 \longrightarrow LiAl(AsH_2)_4 + 4H_2$$

$$LiAl(AsH_2)_4 + 4SiH_3Br \longrightarrow 4SiH_3AsH_2 + LiBr + AlBr_3$$

Trichlorosilane was prepared by passage of HCl, generated in a Kipps apparatus, over Silicon with a $CuCl_2$ catalyst at 300° C, the product being condensed at -78° C.

$$Si + 3HCl \longrightarrow SiHCl_3 + H_2$$

Trifluorosilylchloride and bromide were prepared by cleavage[18] of SiF_3OMe by BBr_3 or BCl_3.

$$SiF_3OMe + BX_3 \longrightarrow SiF_3X + MeOBX_2$$

Trifluorosilane, hexafluorodisilane, trifluoromethylsilane, trifluorovinylsilane, 1:1 difluorosilacyclopent-3-ene and trifluoroallylsilane were prepared by halogen exchange of the corresponding chlorides with antimony trifluoride using an antimony pentachloride catalyst, all except the first occurring at 60° C. Reaction in a packed column

tended to cause decomposition, blackening occurring due to deposition of antimony metal, e.g.

$$SiHCl_3 + 8SbF_3 \longrightarrow 3H_2 + 6SiF_4 + 2Sb + 6SbCl_3$$

Reaction in a 1 litre greaseless tap ampoule using 5 m moles of chlorosilane and an excess of SbF_3 was successful. i.r. and n.m.r. spectra were used to check for purity[19, 20, 21, 22, 23].

Vinyltrimethylsilane was prepared by reaction of trimethyl silyl-chloride with vinylmagnesium bromide in diglyme, i.r. being used to check for purity[24].

$$CH_2 = CHBrMg + SiMe_3Cl \longrightarrow CH_2 = CH - SiMe_3 + MgBrCl$$

Vinyl and allyl germane were prepared by addition of germyl chloride to vinyl magnesium bromide or allyl magnesium chloride in diglyme at 0° C. These Grignards were found to give the best yields although separation of the products from the starting materials was difficult, allyl germane being pumped off allyl chloride at -85° C. The Grignards were formed 'in situ' in a greaseless tap ampoule by shaking magnesium turnings with the halide and a crystal of Iodine in diglyme until the magnesium dissolved. The purity of allyl gemane was checked by i.r. and n.m.r. (see appendix II), and molecular weight determinations, (found 107, required 115), and of vinyl germane by I.R. and vapour pressure determinations at -46° C (found 99 m.m, required 100 m.m)[25].

Trifluoromethylbromide and chloride were prepared by reaction of the corresponding halide with silver trifluoroacetate[23] at 50° C.

$$CF_3\,CO_2^-Ag^+ + X_2 \longrightarrow CF_3X + CO_2 + AgX$$

They were purifed by washing with KOH solution to remove CO_2 and checked by i.r.[26, 27].

Silver Cyanide was precipitated from silver nitrate with potassium cyanide in .880 ammonia solution, to avoid decomposition . After recrystallisation from .880 ammonia the crystals were dried in an oven at 65° F.

Arsine was prepared by addition of water to sodium arsenide in 5 cms Nitrogen pressure.

$$Na_3As + 3H_2O \longrightarrow AsH_3 + 3NaOH$$

The sodium arsenide was prepared by dissolution of its elements in liquid ammonia, trace ammonia being removed from the arsine by washing with water.

Aluminium Iodide was prepared by flaming a mixture of aluminium foil and iodine crystals under vacuum in a greaseless tap ampoule until all iodine was used and colourless crystals were formed.

Boron triiodide was prepared by refluxing iodine with lithium borohydride in n-hexane until the former had all reacted. The solution was filtered in a dry bas and the solvent taken off under vacuum yielding white crystals[29].

$$LiBH_4 + 4I_2 \longrightarrow BI_3 + LiI + 4HI$$

Silve bromide was prepared by precipitation from solutions of silver nitrate and sodium bromide in distilled water.

Hydrogen bromide, bromine, chlorine, iodine, vinyl bromide, allyl halides, methane thiol, trimethylamine, trimethylphosphine, propylene and but-1-ene were all commercial samples, purified by distillation. Various reagents were purified as follows;

Monoglyme - shaken with K/Anthracene

Diglyme - shaken with K/Anthracene

H.M.P.A. - pumped at 150° C

SbF_3 - dried in an over at 80° C for 4 days after thorough grinding

Dimethyl ether - distilled in vacuo

Ammonia - distilled from sodium metal

T.M.S. - spectroscopic grade, distilled

Arcton - commercial grade, distilled

Toluene - analar grade, distilled.

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Photo-Electron Spectra of the Mono and Dihalo Silanes and Germanes

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The photo-electron spectra of the mono and dihalo silanes and germanes show the expected features attributable to various valence-shell energy levels; in some cases clear evidence of ($p \rightarrow d$) π-bonding is observed.

The photo-electron (P.E.) spectra of the halogen derivatives of CH_4 are known [1-3]; we report the P.E. spectra of some of the corresponding silicon and germanium compounds, recorded as part of our investigation of the changes in bonding in similar compounds of the various group 4 elements.[4] A preliminary account of some aspects of this work has appeared earlier.[5]

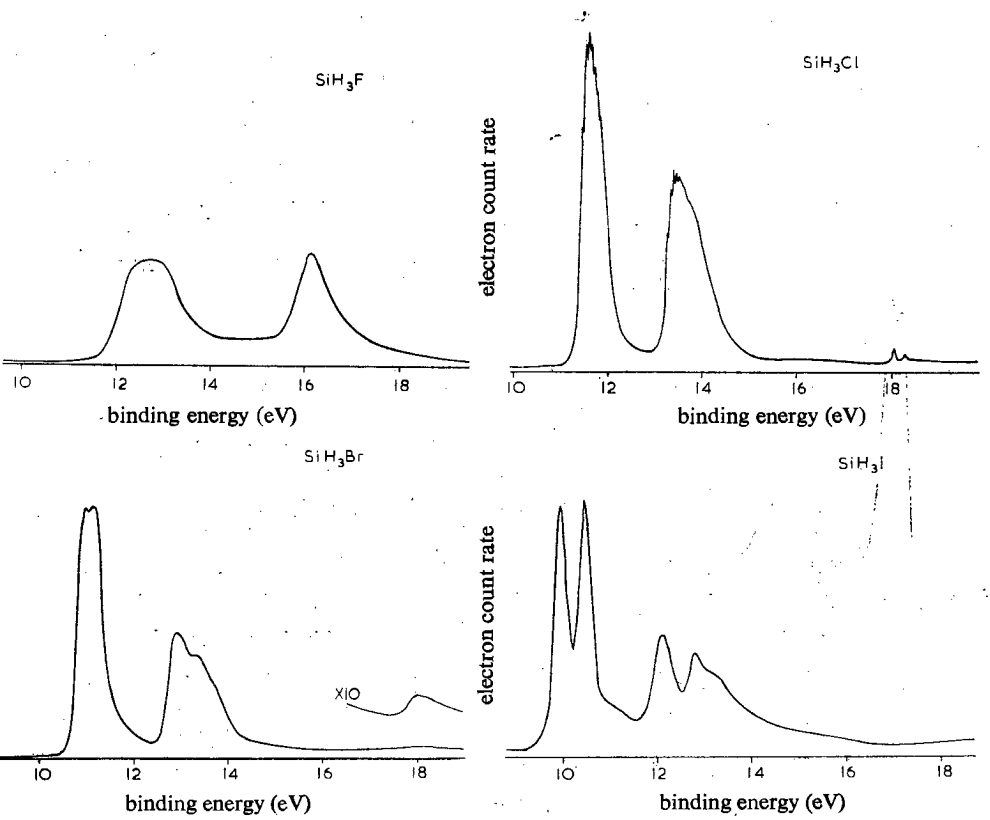

FIG. 1.—The P.E. spectra of SiH_3X. (*a*) X=F, (*b*) X=Cl; (*c*) X=Br; (*d*) X=I.

EXPERIMENTAL

The P.E. spectra were recorded using a Perkin-Elmer PS16 spectrometer with He I (584 Å) excitation. The mono and dihalosilanes and germanes were prepared by standard routes [6] and purified by fractionation in a vacuum line. U.-v. spectra were recorded using a Unicam SP800 spectrophotometer.

RESULTS

The observed vertical ionization potentials are given in tables 1, 2 and 3 together with the corresponding data for the carbon compounds. Spectra are illustrated in fig. 1-4. The suggested assignments of the observed bands are discussed below. We assume throughout the validity of Koopmans' theorem,[7] so that an observed ionization potential (I.P.) is equated with (minus) the corresponding m.o. energy.

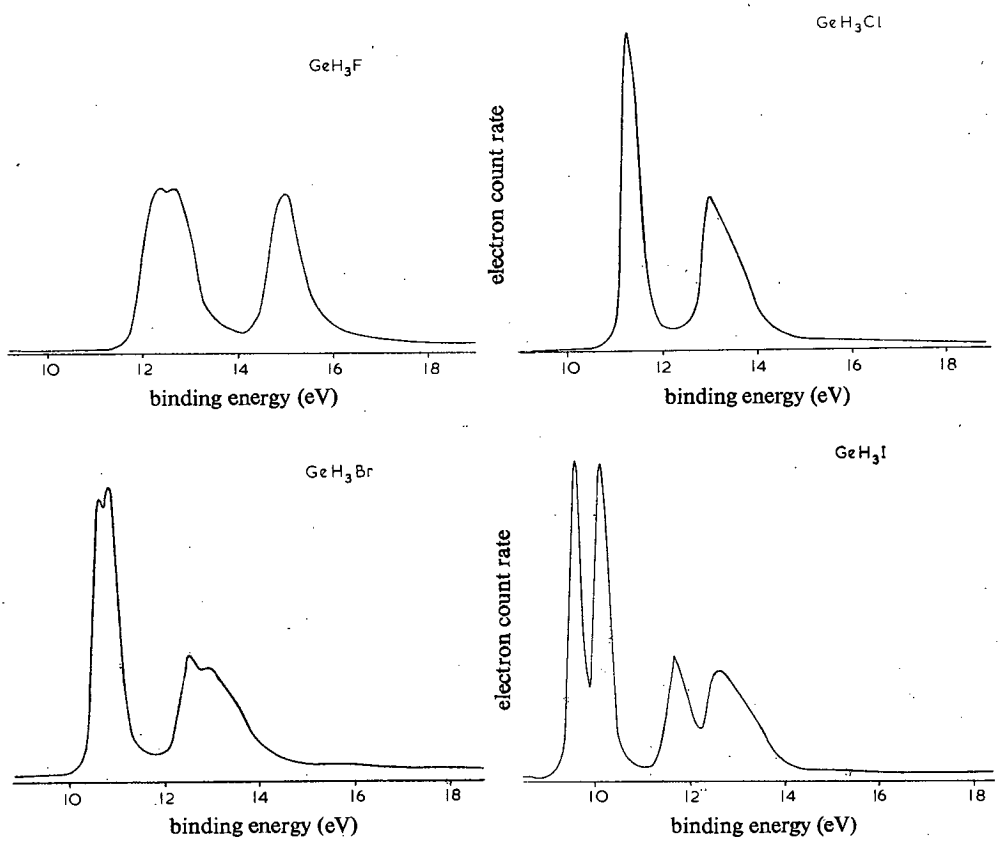

FIG. 2.—The P.E. spectra of GeH_3X. (*a*) X=F; (*b*) X=Cl; (*c*) X=Br; (*d*) X=I.

DISCUSSION

M.O. DESCRIPTION

To facilitate comparison between the C, Si and Ge derivatives we describe only the valence-shell orbitals in each case.

MH_3X

The basis of our description is the set of valence-shell atomic orbitals which may be divided into a_1 and e components as follows:

M	*ns*	a_1			
M	*np*	a_1		M *np*	*e*
H	1*s*	a_1	and	H 1*s*	*e*
X	*n's*	a_1			
X	*n'p*	a_1		X *n'p*	*e*

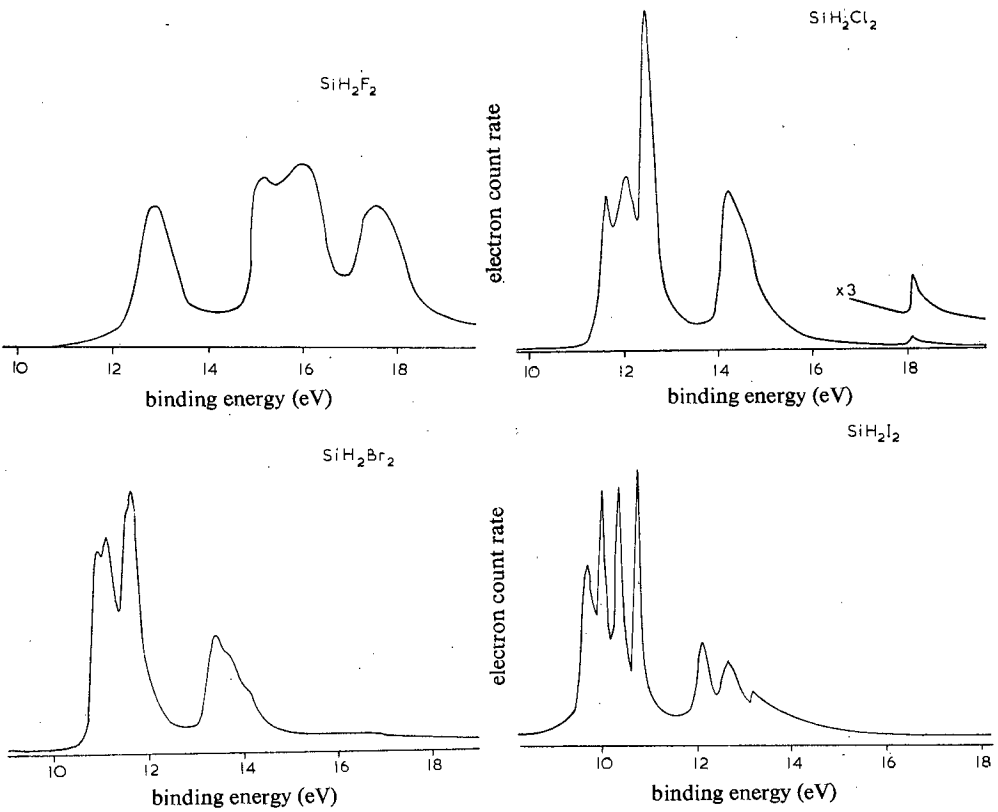

FIG. 3.—The P.E. spectra of SiH_2X_2. (*a*) X=F; (*b*) X=Cl; (*c*) X=Br; (*d*) X=I.

In addition, we may need to consider the *nd* orbitals on M, for M=Si and Ge, which have an a_1 and two *e* components. These will be dealt with separately, the main discussion being based on an m.o. scheme applicable to the carbon compounds.

The five a_1 atomic orbitals will combine to give five a_1 m.o. which may roughly be described as follows:

$5a_1$	MH and MX anti-bonding,
$4a_1$	
$3a_1$	MH and MX bonding,
$2a_1$	
$1a_1$	X *n's* lone pair.

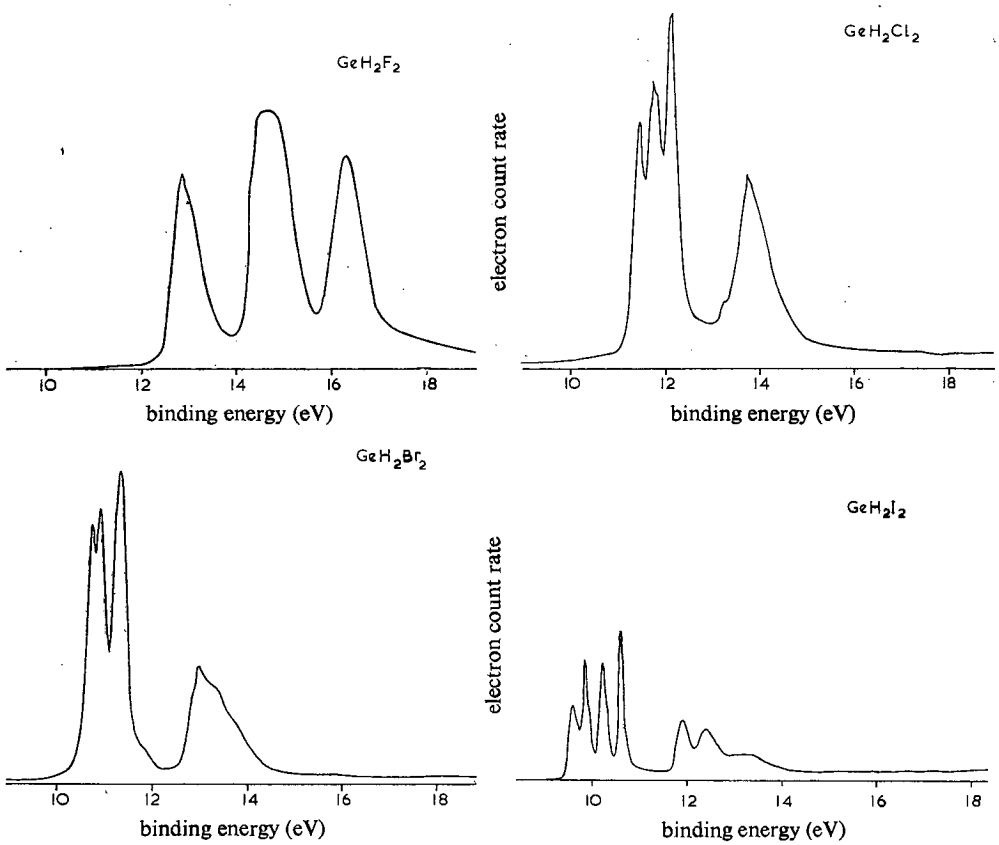

FIG. 4.—The P.E. spectra of GeH_2X_2. (*a*) X=F; (*b*) X=Cl; (*c*) X=Br; (*d*) X=I.

In some cases (e.g., CH_3I) the X *n's* lone pair may actually have a lower I.P. than one of the bonding orbitals, but this is simply a matter of relabelling the orbitals to take account of the relative energies of the constituent atomic orbitals.

The three *e* atomic orbitals will combine to give three *e* molecular orbitals, which for X=Cl, Br and I will have the approximate descriptions:

3*e*	MH anti-bonding,
2*e*	X *n'p* lone pairs,
1*e*	MH bonding.

For X=F, 1*e* and 2*e* will probably exchange character [12] as the F2*p* lone pairs are expected at higher I.P. than the MH bonding electrons. Thus, the expected occupied orbitals are three a_1 and two *e*, needing 14 electrons to fill them. These are supplied as 7 from X, 4 from M and 1 each from 3H.

The presence of unoccupied *nd* orbitals for M=Si and Ge will introduce the possibility of (*a*) participation of a_1 and *e* components of *nd* in the a_1 and *e* bonding levels, and (*b*) (p→*d*) π-bonding from the X *n'p* lone pairs to the *e* components of the *nd* orbitals giving an occupied M—X bonding *e* level (at higher I.P. than the X *n'p* lone pairs), and an unoccupied M—X anti-bonding level. It is difficult to see how the effects of (*a*) could be detected, but (*b*) will lead to the replacement of the

non-bonding X $n'p$ lone pair band by one at higher I.P. with a contour indicating M—X bonding.

MH_2X_2

In C_{2v} symmetry the constituent atomic orbitals may be assigned to symmetry classes as follows:

	a_1	a_2	b_1	b_2
M ns	s			
M np	p_z		p_x	p_y
H $1s$	$Ha+Hb$		$Ha-Hb$	
X $n's$	X_as+X_bs			X_as-X_bs
X $n'p\sigma$	$X_ap\sigma+X_bp\sigma$			$X_ap\sigma-X_bp\sigma$
X $n'p\pi$	$p\pi$	$p\pi$	$p\pi$	$p\pi$
(M nd	d_{z^2}, $d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz})

The separation of the X $n'p$ orbitals into components along the MX bond ($p\sigma$) and perpendicular to the MX bond ($p\pi$) rather than into x, y and z components allows a closer comparison with the MH_3X spectra, the various $p\pi$ orbitals and X $n's$ orbitals being treated as "halogen lone pairs". This leaves four a_1, two b_1 and two b_2 orbitals which will combine to give two bonding (a_1), one bonding (b_1), one bonding (b_2) and the corresponding anti-bonding molecular orbitals.

X p	lone pairs	$4a_1$	$1a_2$	$2b_1$	$3b_2$
M p	bonding	$3a_1$		$1b_1$	$2b_2$
M s	bonding	$2a_1$			
X s	lone pairs	$1a_1$			$1b_2$

This treatment must be modified somewhat for the difluorides, where the F $2p$ lone pairs come at higher I.P. than some of the M p bonding levels, and for CH_2I_2 where we may expect the I $5s$ lone pairs at lower I.P. than the C $2s$ bonding level.

ASSIGNMENT OF BANDS

Treating the chlorides, bromides and iodides together, it is found that the halogen $p\pi$ levels are separated from the bonding levels in all cases, as for the carbon compounds.[1, 2] Spin-orbit coupling appears for the monobromides and mono-iodides making it reasonably certain that the first band in the spectrum corresponds to the $p\pi$ lone pairs. The ionization potentials for the first bands in the spectra of the monochlorides, bromides and iodides, corresponding to the $2e$ m.o., are given in table 1, and discussed below.

TABLE 1.—VERTICAL IONIZATION POTENTIALS FOR MH_3X (eV)

level	X: Cl			Br			I		
M =	C[a]	Si	Ge	C[a]	Si	Ge	C[a]	Si	Ge
$2e$	11.28	11.61	11.30	10.53 10.84	10.96 11.10	10.61 10.83	9.54 10.16	9.78 10.33	9.59 10.14
$3a_1$	14.4	13.4	13.05	13.5	12.85	12.51	12.5	12.04	11.71
$1e$	15.5	13.7	13.3	15.1	13.3	12.9	13.8	12.8	12.6
$2a_1$	—	18.04	—	—	18.1	—	—	—	—
$1a_1$	—	—	—	—	19.5	—	—	—	—

[a] ref. (1); IP ±0.02 or ±0.1 eV, depending on number of figures given.

In the mono-halo methanes the $3a_1$ and $1e$ bonding levels (the first largely CX bonding and the second purely CH bonding), come close together,[1] the a_1 level giving a narrower band than the e level, which is broadened by Jahn-Teller distortion of the ion. In the silane and germane derivatives, the separation between these levels appears to be less than in the methane derivatives and only a single band usually appears. Nevertheless, it is possible in most cases to assign a shoulder at higher I.P. to the $1e$ level, while the main peak which appears to be a narrower band is assigned to the $3a_1$ level.

In SiH_3Cl and SiH_3Br a weak band appears at about 18 eV; the band is sharp for SiH_3Cl and diffuse for SiH_3Br, the vibration frequency excited in the chloride being about 1760 cm^{-1}. The similarity in position, intensity and fine structure to the a_1 bonding level band [8] in SiH_4 leave little doubt that for SiH_3Cl, this band corresponds to the $2a_1$ bonding level, which is essentially Si $3s$—H $1s$ bonding. The diffuseness of the corresponding band in SiH_3Br suggests that the $2a_1$ level here is more involved in SiBr bonding as well as in SiH bonding. A second weak diffuse band appearing in SiH_3Br at an I.P. of 19.5 eV may be due to the $1a_1$ level, essentially a Br $4s$ lone pair.

TABLE 2.—VERTICAL IONIZATION POTENTIALS OF MH_2X_2 (eV)

level	X / M =	Cl C[a]	Cl Si	Cl Ge	Br C[a]	Br Si	Br Ge	I C[a]	I Si	I Ge
X $p\pi$		11.4	11.64	11.42	10.63	10.92	10.69	9.52	9.69	9.56
" lone pairs "		11.5	12.06	11.72	10.83	11.12	10.85	9.83	9.99	9.82
		12.2	12.50	12.08	11.25	11.61	11.28	10.29	10.35	10.18
								10.63	10.73	10.53
M p " bonding "		15.1	14.3	13.76	14.0	13.35	12.93	12.9	12.13	11.89
		15.8	—	—	14.6	13.7	13.17	13.8	12.63	12.32
		16.6	—	—	16.0	—	13.71	15.8	13.24	13.02
M s " bonding "		—	18.12	—	—	—	—	—	—	—

[a] ref. (2).

In the dichloro, dibromo and diiodo compounds (table 2), the halogen $2p$ lone pairs are again at lower I.P. than all the bonding levels and give rise to strong, more or less sharp, peaks. Three bands are found for the dichlorides and dibromides, while all four appear for the diiodides. It is not possible to assign these individually to the expected a_1, a_2, b_1 and b_2 components, though the a_2 level, which cannot interact with any bonding level, might be expected to have the highest I.P. in each case.

The bonding bands at higher I.P. are again less well-separated than in the carbon compounds, and three distinct bands can only be distinguished for GeH_2Br_2, SiH_2I_2 and GeH_2I_2. The order of I.P. would seem likely to be b_2 (MX bonding) $< a_1 < b_1$ (MH bonding) in each case. Only in one case (SiH_2Cl_2) has a weak band attributable to the M s bonding ($2a_1$) orbital been observed.

Assignment of the bands in the spectra (table 3) of the fluorides MH_3F and MH_2F_2 is not straightforward. As for the corresponding carbon compounds,[3] coincidence or near coincidence of several of the energy levels leads to spectra containing fewer bands than expected, and we observe only two bands for MH_3F and three or four for MH_2F_2. For MH_3F it seems clear that neither band can be assigned solely to the F$2p\pi$ lone pairs; both bands must be due to ionization from molecular orbitals that contain contributions from MH_3 bonding and F$2p\pi$ lone pairs.[12] In addition, the $3a_1$ M—F bonding orbital must give a band, probably

concealed by one of the two broad e bands. We consider it more likely that the $3a_1$ band is near the $1e$ band at higher I.P., by comparison with the MF bonding levels in SiF_4 and GeF_4 and have suggested this in table 3. In MH_2F_2 we are confident in assigning the band at lowest I.P. to the MH bonding $1b_1$ orbital, as for CH_2F_2.[3] The band at highest I.P. for SiH_2F_2 and GeH_2F_2 seems likely to be

TABLE 3.—VERTICAL IONIZATION POTENTIALS FOR MH_3F AND MH_2F_2 (eV)

	level	M = C	MH_3F Si	Ge	level	M = C	MH_2F_2 Si	Ge
MH	$2e$	13.1	12.6	12.3	$2b_1$	13.3	12.9	13.0
M-F	$3a_1$	17	16	15	bonding and	15.3	15.2	14.6
					F2$p\pi$ levels	15.7	16.0	
F	$1e$	17.1	16.2	15.0		18.9	17.5	16.3

~18.0 proj.

due to F2p lone pairs; we suggest that it contains both the $1b_1$ level (interacting with $2b_1$ as in CH_2F_2) and the $3a_1$ level, shifted to higher I.P. by π-interaction with the valence-shell d orbitals of Si or Ge. The intermediate band, clearly double for Si but not for Ge, will then correspond to the $1a_2$ and $1b_2$ F lone pair levels and the $4a_1$ and $2b_2$ MF bonding levels. The $2a_1$ (M s bonding) level which is found at 23.9 eV in CH_2F_2 [3] is not observed for SiH_2F_2 or GeH_2F_2; it might be expected roughly mid-way between the positions for MH_4 (18 eV) [8] and MF_4 (21-22 eV),[9] i.e., at about 20 eV, where the sensitivity of our instrument is low.

VIBRATIONAL FINE STRUCTURE

Fine structure corresponding to vibrations of the ion has been observed for only four bands; the first ($2e$) band for GeH_3Cl, and the three bands assigned to the $2e$, $3a_1$ and $2a_1$ levels for SiH_3Cl. The $2a_1$ band for SiH_3Cl shows a progression with a spacing of 1760 cm^{-1} consistent with a reduced SiH stretching frequency as found for the corresponding band in SiH_4.[8] The $3a_1$ band in SiH_3Cl shows a progression of about 6 members with a band frequency of 480 ± 40 cm^{-1}; consistent with a reduced Si—Cl stretching frequency as expected for removal of an Si—Cl bonding electron. The $2e$ bands of SiH_3Cl and GeH_3Cl, as reported earlier,[5] show progressions in a frequency compatible with the M—Cl stretching frequency of the molecule, 520 ± 40 cm^{-1} for SiH_3Cl, ~ 400 cm^{-1} for GeH_3Cl, cf. ground state molecule frequencies of 551 and 423 cm^{-1} respectively.[10] Alternatively, this frequency could be assigned to a much reduced MH_3 rocking frequency, (ground state molecule frequencies of 664 and 602 cm^{-1} respectively).[10] However, we consider this interpretation much less plausible, especially as the rocking mode is not totally symmetric; excitation only by even numbers of quanta is therefore expected. If the assignment as an M—Cl stretching frequency is accepted, then on removing an electron from the $2e$ level, changes in the M—Cl equilibrium bond length will occur. This could occur in two ways: (i) repulsion between Cl lone-pair electrons and MH bonding electrons may be reduced by removal of an electron, thus decreasing the equilibrium bond length; (ii) the $2e$ level may be M—Cl π-bonding, by interaction of the M nd orbitals with the Cl lone-pair orbitals, so that removal of an electron increased the equilibrium bond length.

The first effect would be expected to be greater for C than for Si or Ge because of the shorter CX and CH bonds in CH_3Cl. However, since the $2e$ band in CH_3Cl is quite unlike the $2e$ bands in SiH_3Cl and GeH_3Cl, showing a strong vibrationless component,[1] we conclude that the first effect is not important. The occurrence of

the second effect is consistent with the short M—Cl bonds [11] found for M=Si, Ge and with the trends in I.P. discussed below.

TRENDS IN IONIZATION POTENTIAL

The first atomic ionization potential corresponding to loss of an *np* electron falls sharply from C (11.3 eV) to Si (8.15 eV) and then slightly further to Ge (7.88 eV). We may expect the m.o. containing similar contributions from *np* atomic orbitals to show similar trends, and this is indeed found for most of the assigned levels, notably the $1e$ and $3a_1$ levels for the monohalides and the $3a_1$, $1b_1$ and $2b_2$ bonding levels for the dihalides. Levels localized on a halogen atom would be expected to change the I.P. as M changes because of differing effective charges on the halogen as the electronegativity difference changes. Taking Si and Ge as having roughly similar electronegativities considerably smaller than that of C, we expect the halogen lone pair I.P. to be less for M=Si or Ge than for M=C. However, it is found in every case (except the fluorides), that the halogen lone pair I.P. is greater for the Si compound than the corresponding C compounds. This is most easily explained in terms of $(p\rightarrow d)$ π-bonding between the halogen and silicon which makes the " lone pair " harder to remove. The magnitude of the effect does not appear to decrease by more than a factor of 2 or 3 between the Cl and I compounds. This evidence, combined with that of the change in band shape for the MH_3Cl compounds strongly suggests the occurrence of $(p\rightarrow d)$ π-bonding in these compounds.

CORRELATION BETWEEN I.P. AND BOND ENERGY

Turner *et al.*[1] have pointed out that a monotonic, almost linear, correlation exists between the vertical I.P. for M—X bonding electrons and the M—X thermochemical bond energy for CH_3X (X=Cl, Br, I). A similar correlation has now been found for SiH_3X and GeH_3X and the six points for these compounds fall on a single curve, not the same as that for the carbon compounds.

CORRELATION WITH U.-V. SPECTRA

Although the u.-v. spectra of the methyl halides have been known for a long time,[13] little progress has been made in their interpretation. The original conclusions of Price,[13] that the first band corresponds to an $n\rightarrow\sigma^*$ transition while the next two are best described as the perturbed first members of various Rydberg series, seem to be generally acceptable. The bands are therefore all ascribed to excitation from the halogen *p* lone pairs to various orbitals more or less localized on the halogen atom, with the exception of the first band in each case where the excited state orbital is C—X anti-bonding. A similar explanation seems to account for the overall features observed in the u.-v. spectra of the hydrogen halides,[14] though here more detailed work [15] has revealed the multiplet structure of some bands.

It might be hoped that comparison of the spectra of silyl and germyl halides with those of the methyl halides would throw light on the situation and on any changes that occur as the central atom changes. Unfortunately, only the iodides and GeH_3Br give bands within the range of non-vacuum instruments and only SiH_3Cl seems to have been investigated in the vacuum u.-v.[16] In addition, the changes in band positions involve changes in both upper and lower levels and any discussion of transition energies is difficult to relate to changes in particular levels.

With the identification of the " halogen *p* lone-pair " levels by P. E. spectroscopy, we may now deduce, roughly, the positions of the upper levels from the transition

energies. The results, where transition energies are available, are shown in table 4. Only those transitions designated by Price as A, B and D for CH_3X are shown; for SiH_3Cl, where three similar transitions are observed, the deduced pattern of upper energy levels is similar to that for CH_3Cl, except that the I.P. for each level is

TABLE 4

MH_3Cl	I.P. (2π)(eV)	transition energies (eV) A	B+C	D	upper level I.P. (eV)		
M=C	11.3	7.2	7.9	8.8	4.1	3.4	2.5
M=Si	11.6	8.3	9.3	10.3	3.3	2.3	1.3
M=Ge	11.3		—			—	
MH_3Br							
M=C	10.5	6.1	7.0	8.2	4.4	3.5	2.3
M=Si	11.0	6.5				—	
M=Ge	10.6	6.2			4.4		
MH_3I							
M=C	9.5	4.8	6.1	7.3	4.7	3.4	2.2
M=Si	9.8	5.7			4.1		
M=Ge	9.6	5.1	6.2		4.5	3.4	

about 1 eV less for the Si compound. A similar but smaller raising of the upper energy level is found for the only observed transition in SiH_3I. The energy levels found for GeH_3Br and GeH_3I are much closer to those of the methyl compounds than the corresponding silyl compounds. We have already noted this pattern of behaviour for the halogen p lone pair orbitals and this lends support to the assignment of the upper levels of the observed transitions as mainly concerned with the halogen atom rather than the MH_3 group.

THE P.E. SPECTRUM OF Me_3SiCl

As such interesting effects were found in the spectrum of SiH_3Cl, it was thought pertinent to examine the spectrum of Me_3SiCl to see whether similar results could be obtained. Unfortunately, bands due to ionization of $(CH_3)_3Si$ electrons obscure the region of the spectrum between about 11 and 16 eV. The band we assigned to the Cl p lone pairs appears at about 10.08 eV but it is broad and is almost certainly shifted to lower I.P. by interaction with a level at about 11.9 eV due to the $(CH_3)_3Si$ bonding electrons. No conclusions can therefore be drawn about the existence of $(p\rightarrow d)$ π-bonding in the Me_3SiCl.

CONCLUSIONS

The P.E. spectra of the mono- and di-halo silanes and germanes provide a basis for detailed discussion of their electronic structure. In particular, the evidence in the spectra of silyl and germyl chlorides for the occurrence of $(p\rightarrow d)$ π-bonding is strong. It seems likely, from the observed trends in I.P. of the halogen $p\pi$ lone pair orbitals, that similar bonding occurs in most of the other compounds. Similar conclusions for the fluoro-compounds are precluded by fortuitous interference of the fluorine lone-pair energy levels and the bonding levels, and for Me_3SiCl by a similar interaction of the Cl lone pair levels and the Me_3Si bonding levels.

Footnote—It has been brought to our attention that Prof. W. C. Price, F.R.S. has obtained similar spectra for many of these molecules. His interpretation in terms of π bonding from halogen to M *nd* orbitals is essentially identical to ours.

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Photoelectron Spectra of the Methyl, Silyl and Germyl Derivatives of the Group VI Elements

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Photoelectron spectra of $(MH_3)_2Y$ and MH_3SH (M = C,Si,Ge; Y = O,S,Se,Te) have been observed and the bands assigned to the expected valence-shell energy levels. The results are consistent with the existence of $(p \rightarrow d)$ π-bonding for all the compounds with M = Si,Ge.

As part of our systematic study [1] of MH_3— (M = C,Si,Ge) derivatives we heve obtained photoelectron (P.E.) spectra of the compounds $(MH_3)_2O$, $(MH_3)_2S$, MH_3SH, $(MH_3)_2Se$ and $(MH_3)_2Te$. The spectra now provide an experimental basis for consideration of the bonding in these molecules.

EXPERIMENTAL

P.E. spectra were obtained using a Perkin-Elmer PS16 spectrometer employing He I (21.22 eV) excitation. Compounds were introduced from a glass vacuum system fitted with greaseless taps through a stainless steel inlet manifold. Frequent cleaning of the inlet systems was necessary to prevent metathesis reactions, which apparently occurred readily between some vapour-phase samples and solid decomposition products from earlier samples.

Ultra-violet spectra were obtained with a Unicam SP800 spectrophotometer, using matched 100 mm gas cells.

$(CH_3)_2O$ and CH_3SH were commercial samples, purified by vacuum fractionation. The other compounds were prepared by the reactions shown below.

$$CH_3I + K_2S \rightarrow (CH_3)_2S \text{ in boiling water} \quad \text{ref. (2)}$$

$$CH_3I + K_2Se \text{ or } K_2Te \rightarrow (CH_3)_2Se \text{ or } (CH_3)_2Te \text{ in HMPA}$$

$$SiH_3Cl + H_2O \rightarrow (SiH_3)_2O$$

$$GeH_3Br + Pb(OH)_2 \rightarrow (GeH_3)_2O$$

$$(SiH_3)_3N + H_2S \rightarrow (SiH_3)_2S \quad \text{ref. (3)}$$

$$(SiH_3)_2S + GeH_3Br \rightarrow (GeH_3)_2S \quad \text{ref. (4)}$$

$$(SiH_3)_2S + H_2S \rightleftharpoons SiH_3SH$$

$$(GeH_3)_2S + H_2S \rightleftharpoons GeH_3SH$$

$$SiH_3Br + K_2Se \rightarrow (SiH_3)_2Se \text{ in } (CH_3)_2O \text{ at } 177\ K \quad \text{ref. (5)}$$

$$(SiH_3)_2Se + GeH_3Br \rightarrow (GeH_3)_2Se \quad \text{ref. (5)}$$

$$SiH_3Br + Li_2Te \rightarrow (SiH_3)_2Te \text{ in } (CH_3)_2O \text{ at } 177\ K \quad \text{ref. (6)}$$

$$(SiH_3)_2Te + GeH_3Br \rightarrow (GeH_3)_2Te. \quad \text{ref. (5)}$$

They were purified by vacuum fractionation, and the purity confirmed by infra-red spectroscopy. The thiols SiH_3SH and GeH_3SH could not be obtained free of H_2S, but the proportion of $(MH_3)_2S$ was reduced to the lowest possible level before use.

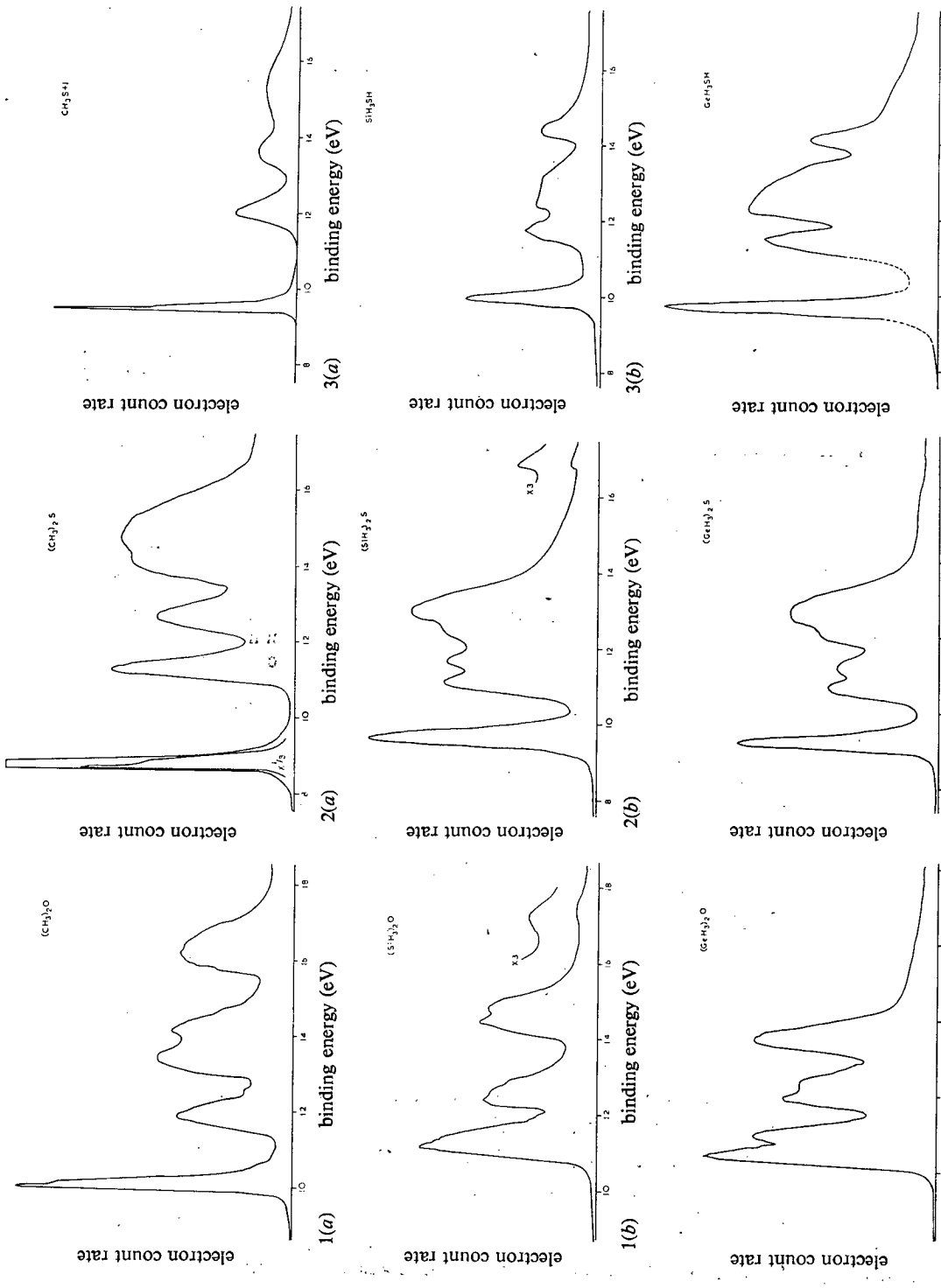

(CH3)2O
(CH3)2S
CH3SH
(SiH3)2O
(SiH3)2S
SiH3SH
(GeH3)2O
(GeH3)2S
GeH3SH
electron count rate
binding energy (eV)
1(a)
2(a)
3(a)
1(b)
2(b)
3(b)

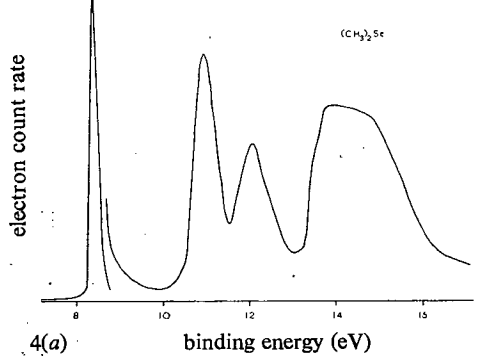
FIG. 1.—P.E. spectra of $(MH_3)_2O$. (*a*) M = C; (*b*) M = Si; (*c*) M = Ge.

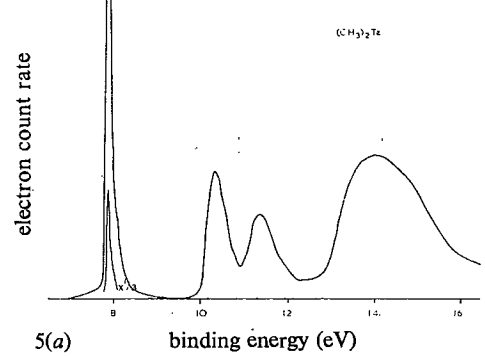
FIG. 2.—P.E. spectra of $(MH_3)_2S$. (*a*) M = C; (*b*) M = Si; (*c*) M = Ge.

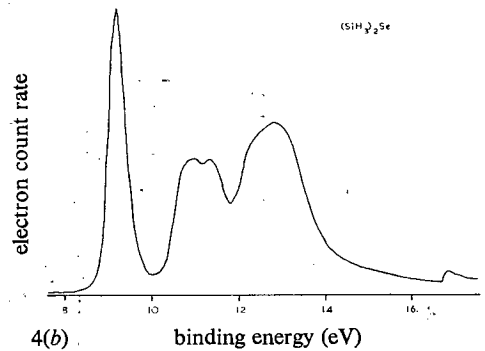
FIG. 3.—P.E. spectra of MH_3SH. (*a*) M = C; (*b*) M = Si; (*c*) M = Ge

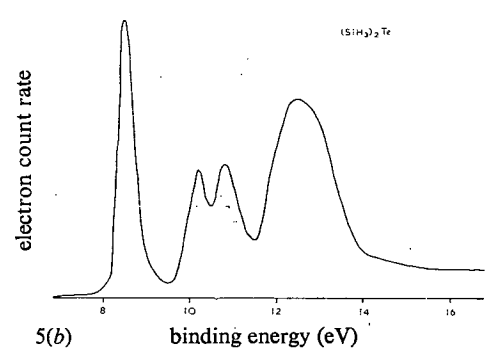
FIG. 4.—P.E. spectra of $(MH_3)_2Se$. (*a*) M = C; (*b*) M = Si; (*c*) M = Ge

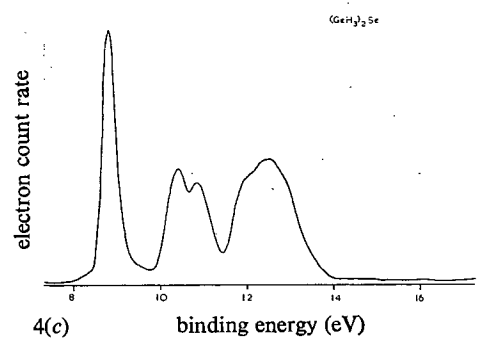
FIG. 5.—P.E. spectra of $(MH_3)_2Te$. (*a*) M = C; (*b*) M = Si; (*c*) M = Ge

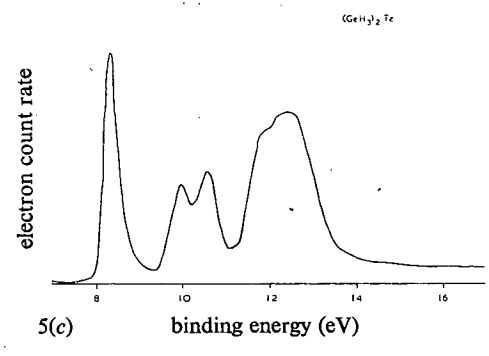












RESULTS

Spectra obtained from the title compounds are shown in fig. 1-5. The vertical ionization potentials (IPs) are listed, with assignments, in tables 1-5.

TABLE 1.—PHOTOELECTRON SPECTRA OF $(MH_3)_2O$

band	O $2p_x$	MH	$3a_1$	$2b_2$	M ns
M = C	10.04	14.2 16.5	11.91	13.43	—
M = Si	11.17	12.5	11.2	14.5	17.2
M = Ge	10.40	2.2	10.9	13.5	—

TABLE 2.—PHOTOELECTRON SPECTRA OH $(MH_3)_2S$

band	S $3p_x$	MH	$3a_1$	$2b_2$	M ns
M = C	8.71	14.5	11.28	12.68	—
M = Si	9.70	12.5	11.15	11.71	16.9
M = Ge	9.25	12.3	10.66	11.30	—

TABLE 3.—PHOTOELECTRON SPECTRA OF $(MH_3)_2Se$

band	Se $4p_x$	MH	$3a_1$	$2b_2$	M ns
M = C	8.40	14.0	11.0	12.0	—
M = Si	9.18	12.5	10.85	11.29	16.75
M = Ge	8.84	12.2	10.44	10.88	—

TABLE 4.—PHOTOELECTRON SPECTRA OF $(MH_3)_2Te$

band	Te $5p_x$	MH	$3a_1$	$2b_2$	M ns
M = C	7.89	14.0	10.35	11.32	—
M = Si	8.63	12.3	10.23	10.83	—
M = Ge	8.34	12.0	9.93	10.56	—

TABLE 5.—PHOTOELECTRON SPECTRA OF MH_3SH

band	S $3p_x$	MH	MS	SH
M = C	9.44	15.1	12.0	13.7
M = Si	9.97	12.5	11.75	14.41
M = Ge	9.69	12.5	11.39	14.08

DISCUSSION

The compounds $(MH_3)_2Y$ have C_{2v} symmetry, and the valence-shell atomic orbitals fall into the following symmetry classes:

atomic orbital	class	a_1	a_2	b_2	b_1
Y $n's$		/			
Y $n'p_z$		/			
Y $n'p_x$				/	
Y $n'p_y$					/
M ns		/		/	
M np_σ		/		/	
M np_π/H $1s$		///	//	///	//
M nd		///	//	///	//

We take the 2-fold axis as z and the plane of the molecule as the yz plane.

The MY bonding involves atomic orbitals of a_1 and b_2 symmetry, principally Y $n'p_z$, $n'p_y$ and M np_σ. Y $n's$ and M ns will of course be involved to some extent, but we believe they will remain sufficiently isolated to retain their atomic labels in the final scheme. The pattern of " skeleton " molecular orbitals in the a_1 class is then:

M np_σ − Y $n'p_z$	M—Y antibonding	$4a_1$
M np_σ + Y $n'p_z$	M—Y bonding	$3a_1$
M ns, Y $n's$		$1a_1$, $2a_1$

In addition there is an a_1 combination of MH bonding orbitals (and corresponding antibonding levels), and a set of three a_1 M nd levels (for Si and Ge). We do not believe that the various MH bonding levels can be distinguished and shall refer to them collectively as " MH ".

In the a_2 class there are only MH bonding and antibonding combinations and two M nd levels.

The b_2 symmetry class is very similar in its contents to the a_1 class, the only difference being the absence of Y $n's$. The " skeleton " molecular orbitals in this class are:

M np_σ − Y $n'p_y$	M—Y antibonding	$3b_2$
M np_σ + Y $n'p_y$	M—Y bonding	$2b_2$
M ns		$1b_2$

In the b_1 class we have MH bonding and antibonding combinations, and M nd levels, as for a_2, and in addition one " skeleton " molecular orbital, $1b_1$, derived from Y $n'p_x$. This is the " Y p lone pair " orbital. (The other lone pair on Y is of course Y $n's$, in symmetry class a_1.)

A similar scheme for MH_3SH, of C_s symmetry, may easily be drawn up. The S $3p$ lone pair level is alone (of the " skeleton " molecular orbitals) in the a'' symmetry class, while the a' contains the following molecular orbitals:

$6a'$	SH antibonding
$5a'$	MS antibonding
$4a'$	MS bonding
$3a'$	SH bonding
$2a'$, $1a'$	S $3s$, M ns

There are MH bonding and antibonding combinations, and M nd levels, in each symmetry class.

The above treatment has ignored Y $n'd$ orbitals; these could be added to the schemes, but we feel it is unlikely that they are involved in bonding in the absence of electro-negative substituents with π-donor properties attached to Y. The ultraviolet spectrum of $(CH_3)_2Te$ suggests that Te $5d$ lies well above Te $6s$ in energy, as in the neutral atom (see below).

In $(MH_3)_2Y$ the occupied orbitals will be $1a_1$, $2a_1$, $3a_1$; $1b_2$, $2b_2$; $1b_1$ and the MH bonding levels. Of these, the M ns levels are observed only for M = Si, and the Y $n's$ level not at all. The ns levels are expected to lie beyond the range of our instrument for M = C [7] and Y = O,S,[8] and are presumably too weak to detect for M = Ge [9] and Y = Se,Te.

The bands we observe for $(MH_3)_2Y$ may be assigned then to the levels: M ns (M = Si only; only one band is observed, which may correspond to both a_1 and b_2

components), $3a_1$ and $2b_1$ (M—Y bonding), MH bonding, and $1b_1$ (Y $n'p$ lone pair). Only in one case are more bands observed than can be accounted for by this scheme. In this instance, $(CH_3)_2O$, we believe that the effective degeneracy of the MH bonding levels is removed by interaction with one of the MY bonding levels. This can only affect the a_1 and/or the b_2 components, which will be shifted in energy while the remaining components will be unaffected.

For MH_3SH we assign the four bands observed in each case to: $3a'$ and $4a'$ (SH and MS bonding), MH bonding, and $1a''$ (S $3p$ lone pair). Si $3s$ was not observed in SiH_3SH, as only a limited amount of compound was available.

DETAILS OF ASSIGNMENTS

Experience with a variety of methyl, silyl and germyl compounds [1] suggests assignment of broad bands near 14.5 eV, 12.5 eV and 12.2 eV respectively to the MH_3 levels. In some cases several overlapping bands seem to be present, but only a single maximum is observed. Only in $(CH_3)_2O$ does there appear to be any gross splitting of this set of levels, due to fortuitous coincidence with one of the CO bonding levels, probably $2b_2$.

The weak bands near 17 eV observed for $(SiH_3)_2Y$(Y = O,S,Se) are confidently assigned as Si $3s$ levels [10]; the shift to lower IP as the electronegativity of Y falls is consistent with the hypothesis that they may be treated as " core levels " whose energy is governed by the net charge on the Si atom.

The band at lowest IP in each molecule is almost certainly to be assigned to $1b_1$ (or $1a''$), the Y $n'p$ lone pair. The measured first IPs for $(CH_3)_2O$ and CH_3SH may be compared with the values of 9.96 eV [11] and 9.44 eV [12] respectively determined from molecular Rydberg series. The first IPs may be compared with those for H_2Y (Y = O,S,Se,Te) [12, 13]; in each series the IP for the parent hydride is greater than that for any of the MH_3— derivatives, and the IPs for MH_3SH are close to the mean of the values for $(MH_3)_2S$ and H_2S. The variation of first IP with M in $(MH_3)_2Y$ is C < Ge < Si in each series, rather than C > Si ⩾ Ge, as might have been expected on the basis of electronegativity changes. The only other occupied orbital of b_1 symmetry is an MH_3 bonding level, but the closer energy match for M = Si,Ge would be expected to lower the IP of the lone pair orbital rather than to raise it. As for the halides and pseudohalides,[1] we can reach no conclusion other than that π-donation from the Y lone pair to the MH_3 group can occur for M = Si,Ge but not for M = C. The most likely orbital for π-acceptance in an MH_3 group would seem to be M nd (b_1). Similar arguments apply for MH_3SH.

The remaining two bands in the spectra of $(MH_3)_2Y$ may now be assigned to $2b_2$ and $3a_1$, the M—Y bonding orbitals. Analogy with the parent hydrides H_2Y [13] suggests that $3a_1$ will be at a lower IP than $2b_2$. For Y = S,Se,Te a pair of bands between $1b_1$ and MH_3 in IP is present in all our spectra; these bands shift with changing M and Y in a manner consistent with their assignment to the M—Y bonding levels.

For Y = O the interpretation is more difficult. For $(GeH_3)_2O$ it seems clear that $2b_2$ and $3a_1$ are on opposite sides of MH_3, $3a_1$ being indeed very close to $1b_1$. For $(CH_3)_2O$ it seems most likely that $2b_2$ has fortuitously coincided with MH_3 near 15 eV, and has mixed with the b_2 component to give two bands at 13.4 eV and 16.5 eV, leaving the remaining components of MH_3 near 14.2 eV. With these patterns in mind a plausible analysis of the $(SiH_3)_2O$ spectrum puts $2b_2$ at 14.6 eV, with $3a_1$ obscured by the lone pair band, $1b_1$, at about 11.2 eV. This is consistent with the pseudo-linear behaviour [14] of this molecule; if the skeleton were linear $1b_1$ and $3a_1$

would coincide, forming a doubly degenerate π_u " O 2*p* lone pairs " orbital, while $2b_2$ would become the main σ_u Si—O bonding orbital. The observed spectrum could indeed be assigned satisfactorily in terms of a linear skeleton. The splitting of the 14.6 eV band is puzzling; the separation of the two components, 0.3 eV, is too large to be any vibration except an SiH stretch, and $2b_2$ is expected to be essentially Si—O bonding, not Si—H bonding. Neither a bent nor a linear skeleton would be expected to give two bands in this region, and Jahn-Teller distortion of the band in a linear molecule would not be expected as the orbital is of σ_u symmetry. The alternative assignment, putting these two components as $3a_1$ and $2b_2$, seems quite unreasonable in view of the pseudo-linear nature of the molecule.

The two remaining bands in the spectra of MH_3SH may be assigned to the M—S and the S—H bonding levels. In each case the band at lower IP is close to the M—S bonding levels in $(MH_3)_2S$ and the band at higher IP is close to the S—H bonding levels in H_2S. The assignment shown in table 5 follows.

VIBRATIONAL STRUCTURE

Only in CH_3SH has any discrete vibrational structure been observed in this set of molecules. The S 3*p* lone pair band in this molecule shows a clear vibrational satellite at $\sim 650\ cm^{-1}$ displacement from the main (0,0) peak. Molecular vibrations [15] of this order are ν(C—S) = 704 cm^{-1} and δ(S—H) = 803 cm^{-1}. However, it is striking that the sharp lone-pair peaks observed for all the carbon compounds are replaced by broader peaks more typical of bonding levels in the Si and Ge compounds. This is consistent with the hypothesis of π-bonding between Si or Ge and the central atom.

ULTRA-VIOLET SPECTRA

The direct observation of the first IP for these molecules affords an invaluable starting-point for analysis of the U.-V. spectra. One approach, particularly applicable to the heavier central atoms Y, is to combine the known term values for the free atoms with the molecular IP to give predicted energies for electronic transitions. Applying this technique to $(CH_3)_2Te$ leads to the prediction of transitions from $1b_1$(Te $5p_x$) to Te 6*s*, 5*d* and 6*p* in the 200-400 nm region. We find three discrete bands in this region, close to the predicted positions, as well as the expected $n \rightarrow \sigma^*$ (Te $5p_x \rightarrow 4a_1, 3b_2$) transitions, as shown in table 6.

TABLE 6.—The ULTRA-VIOLET SPECTRUM OF $(CH_3)_2Te$

observed ν_{max}	assigned upper level	calculated ν_{max}
27 000, 34 000	M—Y antibonding $4a_1$, $3b_2$	
38 800	Te 6*s*	36 300
45 100	Te 5*d*	47 500
49 700	Te 6*p*	48 700

all ν_{max} in cm^{-1}

calculated ν_{max} = (vertical IP)−(atomic term)

The assigned upper levels are consistent with the structures of the bands. The first two bands are completely structureless, showing that the upper states are antibonding. The next band shows a 5-member progression of broad peaks, the vibration frequency being $1100\ cm^{-1}$. The fourth band consists of a large number of

peaks, arranged as a set of progressions in a frequency of 520 cm^{-1} (each progression showing up to 7 members), each progression being displaced from the strongest progression of the set by one of the a_1 vibration frequencies of the molecule.[16] The observed displacements of the more prominent progressions are -190, 0, $+190$, 890, 1240 and 2910 cm^{-1}. This complex structure seems most likely in a level not strongly involved in any particular area of bonding, such as a Te 5*d* level. We have found no evidence for transitions to the Te 4*f* level, expected to be near the 6*s* level. The last observed sharp band is assigned as Te 6*p* on the basis of its position. Any associated structure is obscured by a set of strong continuous bands starting near 46 000 cm^{-1} and probably reaching a peak beyond 50 000 cm^{-1}. These may be due to transitions from bonding to antibonding levels. (e.g., $3a_1 \rightarrow 4a_1$), which are expected in this region.

We hope to extend this analysis to higher energy transitions and to the other molecules as data become available. Preliminary studies on $(GeH_3)_2Te$ show that the 200-400 nm region contains only structureless bands, possibly because of the presence of Ge 4*d* and GeH antibonding levels in the same energy range as the lower excited Te levels, 6*s*, 5*d* and 6*p*.

CONCLUSIONS

The PE spectra of the Group VI derivatives studied here show the expected bands due to valence-shell molecular energy levels.

The variation of Y *p* lone pair IPs and the shapes of the corresponding bands are consistent with $(p \rightarrow d)\pi$-bonding to Si and Ge by all the Group VI elements.

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PHOTOELECTRON SPECTRA OF SOME METHYL, SILYL AND GERMYL AMINES, PHOSPHINES AND ARSINES

Photoelectron Spectra of Some Methyl, Silyl and Germyl Amines, Phosphines and Arsines

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The photoelectron spectra of $(CH_3)_3N$, $(SiH_3)_3Z$, (Z = N, P, As), $(GeH_3)_3N$, $(GeH_3)_3P$, $(SiH_3)_2NCH_3$, $SiH_3N(CH_3)_2$ and MH_3PH_2 (M = C, Si, Ge) are described. In each spectrum the band at lowest ionization potential is assigned to the Z-*p*-orbital that has appreciable lone-pair character. The positions of these bands are consistent with some involvement of this " lone-pair " in bonding to *d*-orbitals of silicon or germanium.

There are some interesting variations in the shapes of the molecules of methyl, silyl and germyl derivatives of nitrogen, phosphorus and arsenic. In all the phosphines and arsines the angle at the Group V atom is little greater than 90°; in trimethylamine the skeletal angle is around 109° and the skeleton in *NN*-dimethylsilylamine is non-planar, whereas the skeletons of *NN*-disilylmethylamine, trisilylamine and trigermylamine are planar. The variations in the shapes of the amines have been interpreted in terms of $(p \rightarrow d)$ π-bonding; it has been suggested that such π-bonding stabilizes the planar geometry by allowing maximum interaction with the lone pair in a pure *p*-orbital. This would be consistent with the weakening basicity of the silylamines with increasing silyl substitution; trigermylamine is too unstable for its basicity to be determined. If the widening of the angle at N were associated with the electron-releasing character of silicon or germanium, the lone pair at nitrogen might be expected to become less tightly bound. In the phosphines and arsines, there is no change in shape, which implies that any π-interaction must be small. On the other hand, the silyl and germyl phosphines and arsines are weak bases. We have therefore investigated the p.e. spectra of some of these molecules.

EXPERIMENTAL

Spectra were recorded using He I (21.22 eV) excitation on a Perkin-Elmer PS16 spectrometer. Experimental conditions were as described earlier.[1-3] Trimethylamine was a commercial sample; other compounds were prepared by standard routes.

The instrument was operated under conditions which allowed complete resolution of reasonably sharp peaks separated by 400 cm^{-1} (50 meV), and partial resolution at 25 meV.

The spectra are illustrated in fig. 1-4. The vertical ionization potentials (for the narrower bands) and the onset-to-tail ranges (for broad bands) are listed in tables 1-4. Table 2 contains the published data [4] for $(CH_3)_3P$ for comparison with our results. Only the first band in the spectrum of $(GeH_3)_3N$ was observed; others were presumably obscured by the strong bands of GeH_3Cl, which was present in excess to retard the otherwise rapid decomposition of the amine.[5]

The only bands to show resolvable fine structure involved ionization of Si(3*s*) or Ge(4*s*) electrons. Such fine structure, though sometimes detected in the spectra of small molecules such as SiH_3CCH, is not generally observed on the main bands in the spectra of such heavy and complex molecules as $(MH_3)_3N$.

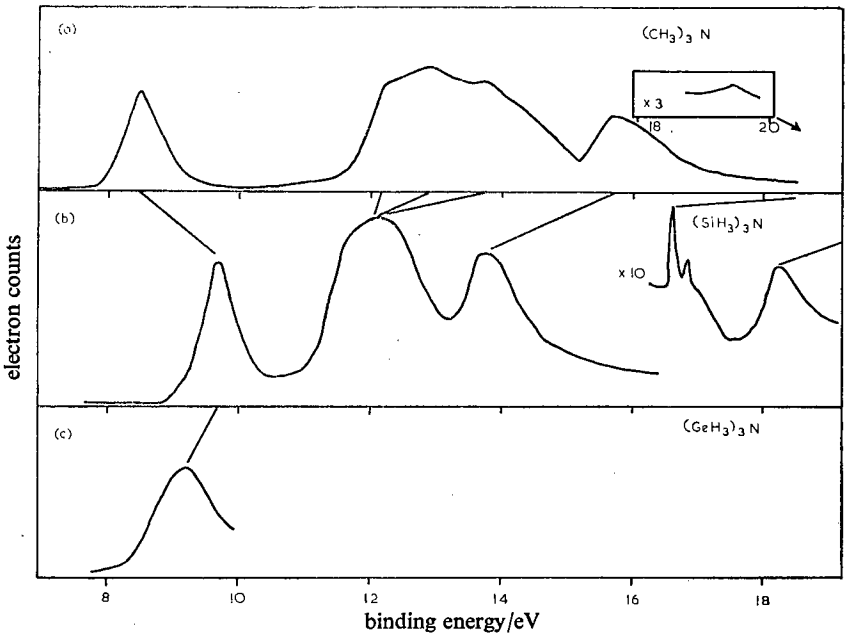

FIG. 1.—Photoelectron Spectra of $(MH_3)_3N$: (*a*) M=C, (*b*) M=Si, (*c*) M=Ge.

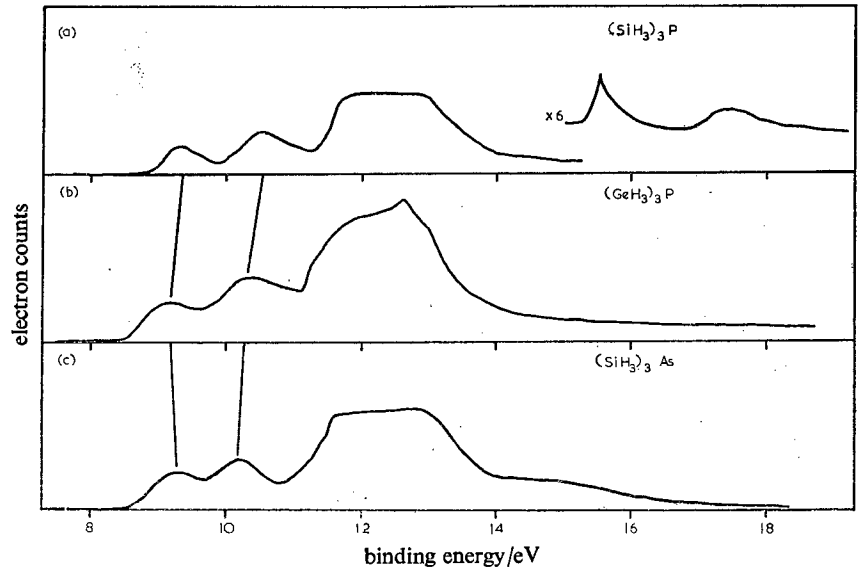

FIG. 2.—Photoelectron Spectra of: (*a*) $(SiH_3)_3P$, (*b*) $(GeH_3)_3P$, (*c*) $(SiH_3)_3As$.

TABLE 1.—PHOTOELECTRON SPECTRUM OF $(MH_3)_3N$

M	$1a_2''$	$2e'$	MH	M ns (a_1')	M ns (e')
C	8.5	15.7	11.6-15	19.4	—
Si	9.7	13.7	10.8-13	16.6	18.2
Ge	9.2	—	—	—	—

All ionization potentials in eV; ±0.1 eV.

TABLE 2.—PHOTOELECTRON SPECTRA OF $(MH_3)_3P$ AND $(SiH_3)_3As$

M	Z	$1a_2''$	$2e'$	MH	M ns (a_1')	M ns (e')
C	P	8.7	11.4	12.7-15.8	—	—
Si	P	9.3	10.6	11.5-13.7	15.6	17.4
Ge	P	9.0	10.4	11.2-13.2	—	—
Si	As	9.3	10.2	11.5-13.2	14.5	—

All ionization potentials in eV; ±0.1 eV.

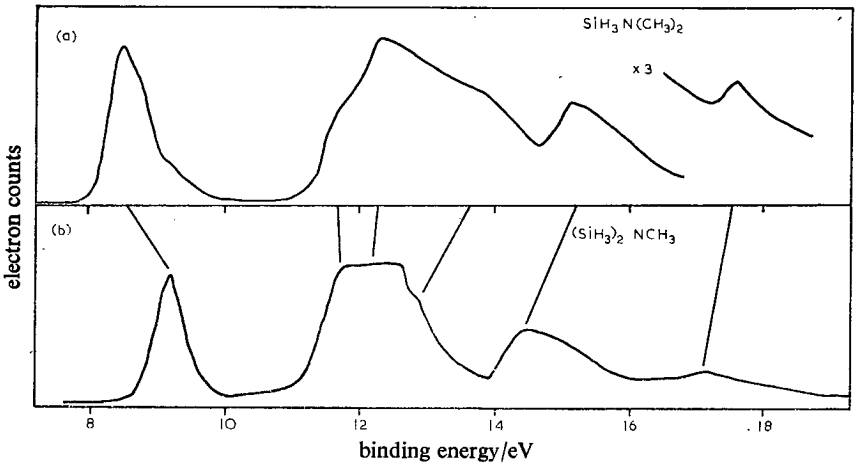

FIG. 3.—Photoelectron Spectra of: (*a*) $(SiH_3)_2NCH_3$, (*b*) $SiH_3N(CH_3)_2$

TABLE 3.—PHOTOELECTRON SPECTRUM OF $(MH_3)_2NM'H_3$

M	M'	N $2p_z$	NC?	MH, M'H, SiN	Si $3s$
C	Si	8.5	15.2	11.1-14.5	17.5
Si	C	9.2	14.4	11.0-13.5	17.0

All ionization potentials in eV; ±0.1 eV.

TABLE 4.—PHOTOELECTRON SPECTRUM OF MH_3PH_2

M	P $3p_z$	MP	MH	PH	M ns
C	9.6	12.4	13.7-16.0	13?	—
Si	9.9	11.6	12.0-13.3	13.6	16.8
Ge	9.7	11.4	11.7-12.8	13.5	16.8

All ionization potentials in eV; ±0.1 eV.

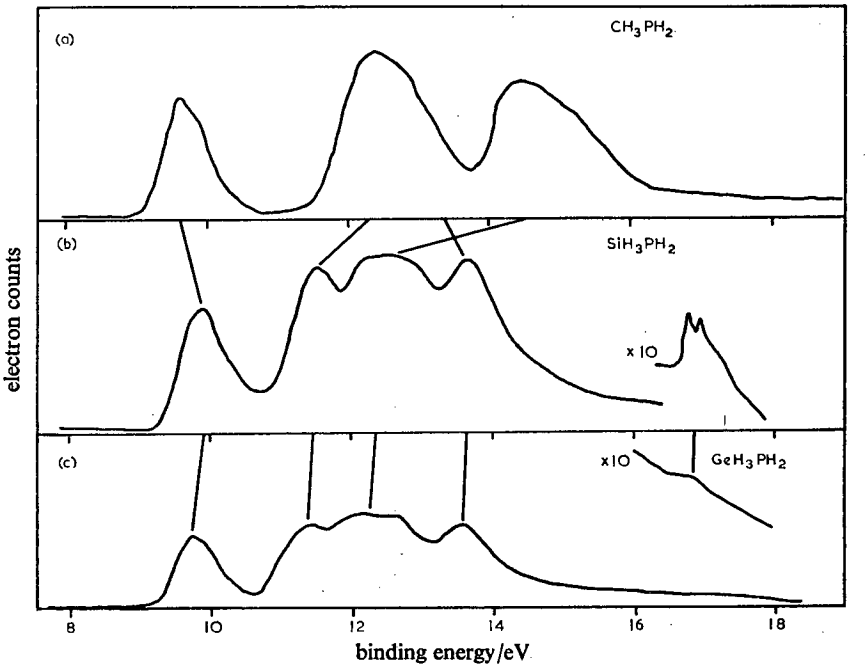

FIG. 4.—Photoelectron Spectra of MH_3PH_2 : (*a*) M=C, (*b*) M=Si, (*c*) M=Ge.

DISCUSSION

TERTIARY AMINES, PHOSPHINES AND ARSINE

In principle it is necessary to consider each molecule separately according to its skeletal symmetry, that is: D_{3h} for $(SiH_3)_3N$ and $(GeH_3)_3N$; (ref. (5), (6)), C_{3v} for $(CH_3)_3N$, $(MH_3)_3P$ and $(SiH_3)_3As$ (ref. (7)), C_{2v} for $(SiH_3)_2NCH_3$ (ref. (8)) and C_s for $SiH_3N(CH_3)_2$ (ref. (9)). The conformations of MH_3 groups are unlikely to produce observable effects in the spectra. In fact, as the spectra illustrated demonstrate, there is no significant difference between the spectra of the more and the less symmetrical molecules, except for the positions of the bands. We shall therefore discuss the electronic structure of a molecule of D_{3h} symmetry, indicating where necessary the differences expected for C_{3v}, C_{2v} or C_s symmetry.

The constituent atomic orbitals are then :

	a_1'	a_1''	a_2'	a_2''	e'	e''
Z $n's$	/					
Z $n'p_z$				/		
Z $n'p_{x,y}$					/	
M ns	/				/	
M np_σ	/				/	
M np_π/H 1s (MH) combinations in all symmetry classes except a_1''						
M nd combinations in all symmetry classes						

For C_{3v} symmetry, the only significant change is that the a_1' and a_2'' classes merge as a_1 ; for C_{2v}, $a_1' \rightarrow a_1$, $a_2'' \rightarrow b_2$, $e' \rightarrow a_1+b_1$, while for C_s, $a_1' \rightarrow a'$, $a_2'' \rightarrow a'$, and $e' \rightarrow a'+a''$. Thus for D_{3h} and C_{2v} symmetry, the Z $n'p_z$ orbital cannot mix with

Z *n's* (or any other orbitals except MH bonding and antibonding levels or M *nd* orbitals), while for C_{3v} and C_s symmetry, Z $n'p_z$ and Z *n's* have the same symmetry and mixing can occur. The lack of any marked discontinuity in the change of binding energy for the highest occupied level in the series $(SiH_3)_3N$—$(SiH_3)_2NCH_3$—$SiH_3N(CH_3)_2$—$N(CH_3)_3$ leads us to suppose that even in the last member the extent of this mixing is small.

Returning to our D_{3h} model, the three skeletal atomic orbitals in the a_1' symmetry class will mix to give

$3a_1'$ M $np_\sigma - $ Z *n's*	MZ antibonding
$2a_1'$ M $np_\sigma + $ Z *n's*	MZ bonding
$1a_1'$ M *ns*	(principally MH bonding).

The extent of the M np_σ/Z *n's* interaction is likely to be small, and $2a_1'$ may well be essentially Z *n's* in character. In this event it will be found at high binding energy and will probably give but a weak band with He I excitation.[10] We do not observe any bands that can plausibly be assigned to MZ bonding (a_1') levels.

In the a_2'' symmetry class we have only a single atomic orbital, Z $n'p_z$, apart from the ubiquitous MH levels and M *nd* orbitals. The observed binding energies of the first bands in our spectra suggest their assignment to this level and the shifts on substitution of Si or Ge for C are consistent with π-donation from Z $n'p_z$ to the available M *nd* orbitals for M = Si, Ge.

In the *e'* symmetry class, the three atomic levels will interact to give:

$3e'$ M $np_\sigma - $ Z $n'p_{x,y}$	MZ antibonding
$2e'$ M $np_\sigma - $ Z $n'p_{x,y}$	MZ bonding
$1e'$ M *ns*	(principally MH bonding).

We believe that $2e'$ will provide the main MZ bonding orbital; M *ns* levels seem on the whole to be MH bonding in MH_3 derivatives.[1, 2]

The occupied orbitals will be $1a_1'$, $2a_1'$; $1a_2''$; $1e'$, $2e'$; and a set of MH bonding levels. Suggested assignments *in these terms* are given in tables 1 and 2, though it must be remembered that for some of the molecules the skeletal symmetry is C_{3v} and $1a_2''$ becomes $3a_1$.

In the p.e. spectra of halides [1] and derivatives of the elements of Group VI [2] we have found some bands which show shapes associated with the ionization of non-bonding electrons. These bands were observed in the spectra of most methyl derivatives; we have observed no bands with these characteristic shapes in the spectra of any silyl or germyl compounds. In the spectra of the amines and phosphines, the only molecules in which the "lone pair" electrons are non-bonding as far as the skeleton are concerned are the planar $(SiH_3)_3N$, $(GeH_3)_3N$, and $(SiH_3)_3NMe$. In the spectra of none of these molecules is a band observed with a "non-bonding" shape. This is not surprising in view of our previous observations; the consequence is that band shapes have not helped our assignments. The absence of resolved vibrational structure we put down to the large number of possible vibrational modes of appropriate symmetry species in these molecules. Our assignments are therefore based on the correlations indicated in the diagrams and on comparison with other model compounds (e.g., NH_3 and PH_3).

For the silyl-*N*-methylamines $(MH_3)_2N$ $M'H_3$ we expect $1a_1'$ and $1e'$ to resolve into two M *ns* levels and one M' *ns* level, while $2a_1'$ and $2e'$ give two MN bonding and one M'N bonding level; the MH bonding levels will also split into MH and M'H sets. The expected splittings are not apparent in the spectra (fig. 3); the inherent breadth of

the bands leads to the appearance of an unresolved group in the range 11-14 eV which presumably contains SiH, CH and SiN bonding levels.

PRIMARY PHOSPHINES

The molecular orbitals for these compounds may be arrived at by a similar procedure. Assuming C_s symmetry, we find only PH and MH bonding orbitals occupied in the a'' symmetry class. The four occupied a' orbitals will be more or less adequately described as P 3*s*; M *ns*; MP σ-bonding; P $3p_z$ in order of decreasing binding energy, except that, for M = C, M *ns* will occur at higher binding energy than P 3*s*.

In the spectra of SiH_3PH_2 and GeH_3PH_2 four strong bands appear between 9 eV and 15 eV (fig. 4); we assign these as shown in table 4. Weaker bands near 17 eV are assigned to M *ns*. For CH_3PH_2, only three strong bands appear; analogy with spectra of other CH_3 compounds suggests assignment of CH near 14.5 eV, while CP and PH are probably both included in the unexpectedly broad band near 12.5 eV. The vertical ionization potentials of the first bands in these spectra, assigned to the P 3*p* lone-pair orbital, show the order C < Ge < Si, as for $(MH_3)_3N$ and $(MH_3)_3P$.

CONCLUSIONS

The p.e. spectra of the compounds studied here cannot be analysed as fully as those of the MH_3 derivatives of the elements of Groups VI and VII, whose spectra we have previously described, mainly because the molecules described in this paper are larger and the broad bands due to the different energy levels may overlap. Nevertheless, we have confidently assigned the band at lowest ionization potential in each spectrum to ionization from the "lone pair" orbital described as Z $n'p_z$. In each series of compounds $(CH_3)_3Z$, $(SiH_3)_3Z$, $(GeH_3)_3Z$ or CH_3PH_2, SiH_3PH_2, GeH_3PH_2 the trend is clear: the order of I.P. is $CH_3 < GeH_3 < SiH_3$. This order is consistent with the suggestion that the lone pair electrons interact with empty *d*-orbitals of Si or Ge; the interaction cannot strictly be described as π-bonding in molecules with non-planar skeleton, but interaction with empty *d*-orbitals of appropriate symmetry is possible in all cases. The ionization potentials we have determined also correlate with the relative basicities of the compounds; they show that the weakly basic character of silyl amines and phosphines is due at least partly to high ionization potentials and should not be explained exclusively in terms of lattice energies or solvation or steric effects.

We are grateful to Dr. D. W. H. Rankin for his advice and assistance in the preparation and handling of $(GeH_3)_3N$, and to the S.R.C. for grants to R. A. W. and for the purchase of equipment.

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Photoelectron Spectra of Some Simple Fluorosilanes

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Photoelectron Spectra of Some Simple Fluorosilanes

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The photoelectron spectra of SiF_3H, SiF_3X (X = Cl or Br), and SiF_3Me excited by He(I) and He(II) radiation are described, with the He(I) spectrum of Si_2F_6; assignments of bands to molecular energy levels are based on comparison with the spectra of related compounds.

We have recently described [1] the He(I) photoelectron spectra of SiH_3X and found evidence in the spectra for ($p\rightarrow d$) π-bonding from X to Si. It has been suggested [2] that π-interactions of this kind are likely to be enhanced by the presence of electronegative substituents at silicon. We have therefore recorded the spectra of SiF_3H, SiF_3Cl, and SiF_3Br, with those of SiF_3CH_3 and Si_2F_6, and assigned the peaks observed by comparison with the spectra of MF_4 (M = C or Si), CF_3H, and CF_3X. The spectra of MF_4 [3-6] and the other fluorocarbons [6,7] have been reported previously.

EXPERIMENTAL

Compounds were prepared by standard routes (1) [8] and (2) [9] in a conventional Pyrex vacuum system. SiF_3H, Si_2F_6, and SiF_3Me were prepared [10] from the corresponding

$$SiF_3OMe + BX_3 \longrightarrow SiF_3X + MeOBX_2 \ (X = Cl \text{ or } Br) \quad (1)$$

$$AgCO_2CF_3 + X_2 \longrightarrow CF_3X + CO_2 + AgX \ (X = Cl \text{ or } Br) \quad (2)$$

chlorides by fluorination with SbF_3. Samples were purified by trap-to-trap distillation and the purity checked by i.r. spectroscopy with a Perkin-Elmer 457 spectrometer, and by molecular weight determinations. The He(I) (584 Å) spectra were recorded by means of a Perkin-Elmer PES 16 spectrometer and He(II) spectra recorded at Perkin-Elmer Ltd.

Assignments.—The compounds SiF_3H and MF_3X belong to the point group C_{3v}. For MF_3X the valence-shell

TABLE 1

Symmetry classes of the valence-shell atomic orbitals of MF_3X

	a_1	a_2	e
M ns	1		
M np_z	1		
M np_x/p_y			1
F $2p_z$	1		1
F $2p_x/p_y$	1	1	2
X xp_z	1		
X xp_x/p_y			1

atomic orbitals can be assigned to symmetry classes as in Table 1, and combined to give the occupied molecular orbitals set out in Table 2; the order of Si–F σ- and F lone-pair levels is not of course determined by symmetry, and depends on the analysis of the observed spectra (see below). However, the order given in Table 2 is at least chemically

TABLE 2

Symmetry classes of the occupied molecular orbitals of MF_3X

	a_1	a_2	e
X $xp\pi$ lone pair			$4e$
Si–X σ	$3a_1$		
F $2p\pi$ lone pair	$2a_1$	$1a_2$	$3e$, $2e$
Si–F σ	$1a_1$		$1e$

plausible. For SiF_3H there is no $4e$ level and $3a_1$ becomes the Si–H σ-level. The spectra are shown in Figures 1 and 2, and the positions of the bands are summarised in Table 3; all the expected valence-shell bands for SiF_3H and SiF_3X are observed in the range 6—21·22 eV.

For SiF_3Me we assume that the appropriate point group is C_{3v}; the Si–C σ-bonding level is $4a_1$, the C–H bonding levels are $4e$ and $1a_1$, the SiF_3 σ-bond levels become $2a_1$ and $1e$, and the fluorine lone pairs $3a_1$,$1a_2$ and $3e$,$2e$. The point group for Si_2F_6 is taken as D_{3d}, with a centre of symmetry; apart from the Si–Si level, a_{1g}, all other levels for the SiF_3 groups split into g and u components.

Our assignments are based partly on analogy with MH_3X, partly on comparison with previous studies of CF_3X and CF_3H, and partly on comparison with the spectra of CF_4 and SiF_4. The spectra of the two tetrafluorides are well known.[3-6] There has been some disagreement about details of the assignments, but it seems clear that the peaks between 15 and 19 eV correspond with ionisation from the t_2,t_1, and e levels that are largely fluorine lone-pair in character, while the next two peaks represent the t_2 and a_1 M–F bonding levels. Most of the discussion about assignments has been concerned with the order of the fluorine lone-pair levels; it is striking that the pattern of the peaks between 15 and 19 eV is much the same in SiF_4 and CF_4, implying that the ordering of levels in the two molecules is probably also the same.

In the spectra of SiF_3Cl and SiF_3Br, the first band is assigned to ionisation from the π-lone-pair levels of the halogen atom, $4e$; in each spectrum the band is relatively sharp, and shows no resolved vibrational structure, being much the same in half-width as the corresponding band in CF_3X. The second band in each spectrum is assigned to

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ionisation from the a_1 Si–X σ-bonding level, and these correlate with the first band in the spectrum of SiF_3H (assigned as for [5] CF_3H to $3a_1$, the σ MH level). In the spectra of MF_3H and MF_3X there follow three bands whose positions, shapes, and relative intensities do not vary a great deal across the whole series of six compounds. These peaks are assigned to the levels $1a_2$, $3e$, and $2e$, all essentially fluorine $2p$-lone-pair in character. While no feature of the spectra indicates which band is associated with which level, the peak in each spectrum at lowest ionisation potential has been assigned to the $1a_2$ because this orbital is weakly antibonding between all fluorines; calculations for CF_3H lead to the same assignment.[5]

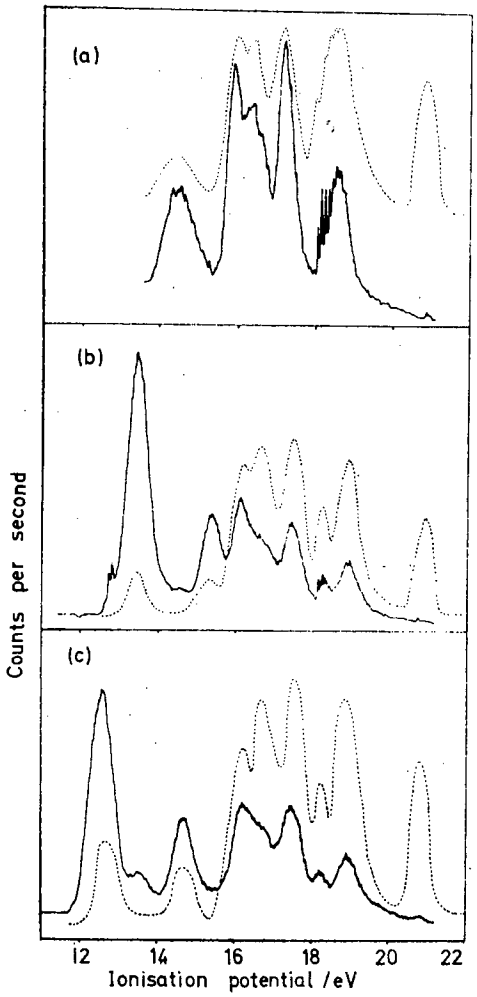

FIGURE 1 The photoelectron spectra of (a), SiF_3H; (b), SiF_3Cl; and (c), SiF_3Br excited by He(I) (——) and He(II) (– – – –) radiation

There remain the MF σ-bonding levels (e and a_1) and the a_1 fluorine lone-pair level. In CF_3H, the a_1 MF σ-bonding level is assigned [5] by analogy with CF_4 and from calculations to the band at 24·4 eV. In CF_3Cl and CF_3Br, the corresponding bands would be expected to fall well outside the He(I) range; we have no data for these compounds beyond 21·2 eV. For CF_3H, the band at 20·5 eV covers both $1e$ and $2a_1$ levels; in CF_3Cl one shifts to 20·15 and the other to 21·0 eV, while in CF_3Br the higher level has shifted to 19·8 eV and the lower level has shifted outside the He(I) range. In view of the sensitivity of both these levels to the nature of the other atom bound to CF_3 we cannot say which represents the $1e$ and which the $2a_1$ level. In the spectra of the silicon compounds, the situation is somewhat different. In each spectrum three bands are observed, one near 18, one near 19, and one just below 21·0 eV. The relative intensities of the first and the third are much in-

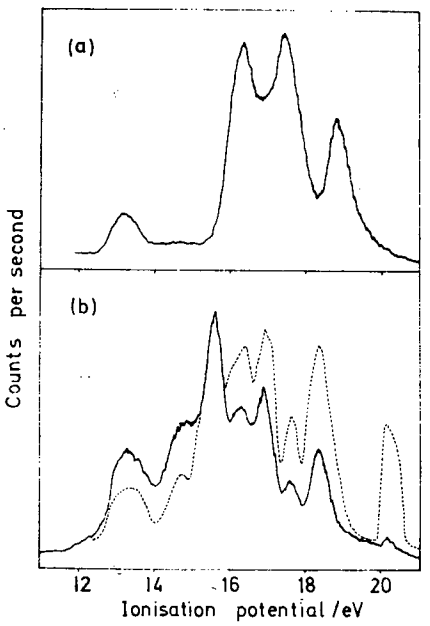

FIGURE 2 The photoelectron spectra of (a), Si_2F_6 and (b), SiF_3Me

TABLE 3

Vertical ionisation potentials/eV (±0·02 eV)

X =	CF_3X			SiF_3X			SiF_3Me		Si_2F_6	
	Br	Cl	H (ref. 5)	Br	Cl	H				
$4e$	12·12	13·08		12·46	13·44		$4a_1$	13·24	$3a_{1g}$	13·20
$3a_1$	14·26	15·15	14·80	14·55	15·33	14·48	$4e$	14·82	$2a_{2g}/3a_{1u}$	16·24
$1a_2$	15·78	15·82	15·5	16·10	16·35	15·94	$1a_2$	15·55	$2e_g/2e_u$	17·31
$3e$	16·51	16·56	16·2	16·63	16·70	16·38	$3e$	16·25	$2a_{1g}/2a_{1u}$	17·85 (shoulder)
$2e$	17·42	17·53	17·24	17·36	17·49	17·24	$2e$	16·84	$1e_g/1e_u$	18·75
$2a_1$	19·8	20·1	19·84	18·10	18·26	18·20	$3a_1$	17·53		
$1e$		~21·0	19·84	18·80	18·92	18·61	$1e$	18·30		
$1a_1$			24·44	20·80	20·86	20·94	$2a_1$	20·14		

creased in spectra excited with He(II) radiation, implying that both these levels have substantial *s*-character [6] and are therefore of a_1 symmetry. We presume that there is substantial mixing between the Si–F σ-bonding and the fluorine lone-pair a_1 levels, and this conclusion is borne out by the vibrational progressions associated with the bands. For SiF_3H and SiF_3Br, the band at 18 eV shows a single progression (see Table 4) in a frequency assigned to a slightly

TABLE 4

Vibrational progressions excited in the $1a_1$ and $2a_1$ levels of the compounds SiF_3X (X = H, Cl, Br, or Me). The values are quoted to ± 40 cm^{-1}

	$2a_1$/cm^{-1}	$1a_1$/cm^{-1}	Molecular vibration frequencies/cm^{-1}	
SiF_3H	790	725	998	νSiF [a]
		330	858	
			425	δSiF_3
SiF_3Cl	965	890	1000	νSiF [b]
	605	200	880	
			596	νSiCl
			345	δSiF_3
SiF_3Br	850	755	1000	νSiF [b]
		240	867	
			330	δSiF_3
SiF_3Me	730	845		
		325		

[a] Ref. 11. [b] Our observations and assignments. Details to be published.

reduced [8,11] Si–F stretching mode. For SiF_3Cl this band shows two progressions. One involves ν(Si–Cl) effectively unchanged from the molecule; the other (965 cm^{-1}) is between the two Si–F stretching frequencies of the molecule,[8] implying either that the symmetric mode is at the higher frequency or that this level is Si–F *anti*-bonding. The progressions associated with the bands near 21 eV are assigned to νSiF and δSiF, all reduced (except for νSiF of SiF_3Cl, which is almost unchanged) from corresponding frequencies of the molecules. The bands near 19 eV show no resolved fine structure, and are assigned to $1e$ (Si–F σ-bonding).

The assignments discussed above also lead to the assignments for SiF_3Me and Si_2F_6. For SiF_3Me the band at lowest ionisation potential is assigned to ionisation from the $4a_1$ (Si–C σ-bonding) level and the next to the $4e$ (C–H bonding) level. The remaining levels follow as described above. For Si_2F_6, the band at lowest ionisation potential is assigned to $3a_{1g}$ (Si–Si σ-bonding); the three bands associated with fluorine lone-pair levels show no splittings, and the only difference between this spectrum and the others so far described is that there is no band just below 21·2 eV. We assume that $1a_{1g}/1a_{1u}$ are beyond the He(I) limit; we were unable to obtain a spectrum of this molecule excited by He(II) radiation.

DISCUSSION

It is interesting to compare ionisation potentials in the molecules studied in this paper with those of related derivatives, in particular MH_3X, M_2H_6, and Si_2Cl_6. The influence of the fluorine substituents might be expected to appear in three ways. Such electronegative groups are likely to increase the binding energies of σ-levels, in particular of the Si–X, Si–H, or Si–Si σ-bonding electrons; this kind of effect has been described as the perfluoro-effect in perfluoro-organic compounds.[12] There will be a similar but smaller effect on π-levels such as $4e$ (π-lone pair of X) of SiF_3X. Secondly, the MF bonding and antibonding levels themselves will interact with other molecular orbitals, and the interaction will differ from similar interaction with MH or MH* levels. Thirdly, the *d*-orbitals of Si will be contracted by the increased effective nuclear charge of the silicon, and so might well become more available for ($p \rightarrow d$) π-bonding from π-lone pairs of X to silicon but not of course carbon.

In addition to all this there is the possibility of ($p \rightarrow d$) π-bonding from fluorine lone pairs to silicon.

It is possible to look for evidence for all these effects in the spectra described here. There can be no doubt of the first effect: the σ-levels are much more tightly bound in MF_3H, MF_3X, or Si_2F_6 than in corresponding compounds containing MH_3 groups; there is even a large shift in the ionisation potential of the Si–Si σ-bond from Si_2Cl_6 to Si_2F_6 (see Table 5). In MF_3X, as in

TABLE 5

Ionisation potentials/eV ($\pm 0{\cdot}02$ eV) of MY_3X (M = Si or C, Y = F or H, and X = Cl or Br)

	SiH_3X	SiF_3X	CH_3X	CF_3X
Cl $p\pi$ lone pair	11·61	13·44	11·28	13·08
Si–Cl σ	13·4	15·33	14·4	15·15
Br $p\pi$ lone pair	10·96	12·46	10·53	12·12
Si–Br σ	12·85	14·55	13·5	14·26
	Si_2H_6	Si_2Cl_6	Si_2F_6	
Si–Si σ	10·60	10·79	13·20	

MH_3X, the lone-pair ionisation potential of X is higher when M = Si than when M = C, and this may well be due, at least in part, to ($p \rightarrow d$) π-bonding to silicon. However, there is nothing in the spectra of SiF_3X to provide more compelling evidence in support of the idea of ($p \rightarrow d$) π-bonding. On the contrary, one feature of the spectra of MH_3Cl and MH_3Br is absent from the spectra of the perfluoro-analogues. The band due to ionisation from the π-lone-pair level of X in MH_3X is sharp and shows no vibrational progression for M = C; when M = Si, the bands are broad and for the chloride show a progression in ν(Si–Cl), slightly reduced from its value in the free molecule. This strongly suggests that the π-lone pairs of X are involved in the Si–X but not to nearly the same extent in the C–X bonds. In the spectra of MF_3X the corresponding bands are all fairly sharp, and show no vibrational progressions; in particular there is no marked change in width from M = C to M = Si. Therefore there is no evidence from band shapes for interactions peculiar to the silicon compounds.

Finally it is interesting to consider the interpretations of the relatively small changes in ionisation potentials

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of at least three of the fluorine lone-pair levels in MF_3Cl and MF_3H. The shifts can be interpreted in two ways: either the fluorine lone pairs are more-or-less unaffected by changing M from C to Si, or the relative constancy of the ionisation potentials reflects a balance of σ-electron release from silicon leading to a lower binding energy, and π-electron donation to silicon which increases the binding energy. It is clear from the increase in the binding a_2 level from CF_3X to SiF_3X that other factors may be involved, for there are no *d*-orbitals of a_2 symmetry.

In summary, it is possible to make fairly complete assignments for the spectra of SiF_3H and SiF_3X; the spectra of the more complex molecules SiF_3Me and Si_2F_6 correlate well with them. However, no firm conclusion can be drawn about the importance of *d*-orbitals in bonding from the spectra of the silicon compounds.

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